4392 *J. Phys. Chem. A* **1997,** *101,* 4392−4401

Atmospheric Oxidation Mechanism of *n*-Butane: The Fate of Alkoxy Radicals

Tim P. W. Jungkamp,[†] James N. Smith,[†] and John H. Seinfeld*,[‡]

Department of Environmental Engineering Science and Department of Chemical Engineering,
California Institute of Technology, Pasadena, California 91125

Received: January 14, 1997; In Final Form: April 3, 1997[⊗]

The atmospheric oxidation mechanism of *n*-butane is investigated by means of density functional theory and *ab initio* calculations. Calculation of energies of reactants, transition states, and stable intermediates predicts the detailed pathways leading to experimentally observed products of *n*-butane oxidation. Also serving as a model system for the oxidation of larger alkanes, quantitative information is obtained for elementary reaction steps that heretofore have been subject to speculation. Complete basis set model chemistries CBS-4 and CBS-q were used with B3LYP/6-31G(d,p) optimized geometries to calculate energies of over 70 stable species and transition states. Energies based on density functional theory were obtained at the B3LYP/6-311+G-(3*df*,2*p*)//B3LYP/6-31G(d,p) level of theory. The principal pathway following formation of the 1-butyl radical from hydroxyl (OH) attack on *n*-butane is found to be 1,5-H shift of the 1-butoxy radical. After conversion to the δ-hydroxy-1-butoxy radical, another 1,5-H shift is expected to be the primary route to 4-hydroxy-1-butanal. 4-Hydroperoxy-1-butanal can be formed after 1,6-H shift in chemically activated 4-hydroxy-1-butylperoxy radicals. Whereas β-scission in 1-butoxy is an endothermic process, fragmentation of 2-butoxy into C_2H_5 and CH_3CHO is predicted to be the major degradation pathway of the secondary butyl radicals.

1. Introduction

Atmospheric reactions of the butoxy radicals ($C_4H_{10}O$) have been the subject of numerous investigations in recent years.[1−8] A key intermediate in the photooxidation of *n*-butane in the troposphere,[9] the 1-butoxy radical is the simplest alkoxy radical that can undergo isomerization via 1,5-H shift to create a δ-hydroxyalkyl radical forming numerous subsequent products. 1-Butoxy and 2-butoxy are thus representative of a large class of alkoxy radicals that are produced by the photooxidation of $>C_4$ aliphatic hydrocarbons in the troposphere and whose fate determines the ultimate end products of these reactions.

The mechanism for the production of butoxy radicals from *n*-butane (Figure 1) in a NO_x−air mixture[9] reveals the complexity involved in the primary oxidation steps of even a small C_4 hydrocarbon. Like all simple alkanes, *n*-butane is expected to be consumed in the troposphere almost exclusively by reaction with hydroxyl radical (OH) to form either of two isomers of the butyl radical. Butyl peroxy radicals will be formed by reaction with O_2, and NO/NO_2 conversion or self-reaction of the peroxy radicals leads to butoxy radicals. A number of experimental studies have been carried out with butoxy radicals in various bath-gas mixtures, including N_2/O_2 mixtures at various O_2 partial pressures and NO_x−air mixtures.[1−8] These product studies have led to proposed reaction mechanisms summarized in Figures 2 and 3. The 1- and 2-butoxy radicals formed are expected to proceed via three degradation channels, as recently reviewed by Atkinson:[10] reaction with O_2 with formation of the corresponding butyraldehydes, β-scission, *i.e.,* unimolecular decomposition by C−C bond cleavage in β-position to the radical center, and isomerization by 1,*n*-H shift, ($n = 4$ or 5). The relative importance of these competing reaction steps is a primary focus in the current study, for it determines the ultimate end products of these atmospheric reactions. For the atmospheric fate of *n*-butane, the reactions of 2-butoxy are more important, with a branching ratio for 2-butyl radical formation from initial OH attack on *n*-butane of 0.85.[9] From a mechanistic point of view, 1-butoxy is the more interesting since isomerization as major reaction pathway is important.

Experimental studies of such systems suffer, in general, from two limitations. The first is the inability of most analytical procedures to distinguish structural isomers despite the use of powerful techniques such as API-MS/MS,[1] although these techniques allow the detection of labile multifunctional carbonyl compounds that are not detectable by classic GC/MS techniques. Perhaps more importantly, most of the studies performed to date could not completely quantify the products and detect intermediates in the reaction sequence. For example, in the case of the two most recent studies on butane oxidation, Kwok *et al.*[1] report the formation of δ-hydroxybutanal, whereas this product is neither observed nor considered as a product by Heiss *et al.*[3] Conversely, Kwok *et al.* did not identify hydroperoxides as products, a major class observed by Heiss *et al.* An additional problem with experiments is frequent lack of authentic standards for these multifunctional compounds, although advanced analytical techniques allow structure determination of products. As a recent example, use of GC/CI−MS/MS and GC/NMR made it possible to identify a hydroperoxy carbonyl compound and its cyclization product as a product of 1-butoxy oxidation.[11] The question of whether the reaction channel leading to hydroperoxide formation presents a thermodynamically possible degradation pathway is addressed in this work through investigation of energies of intermediates and barrier heights.

A few investigators have focused on the problem of determining rate constants and branching ratios of the three possible reaction channels following formation of butoxy radicals. In general, the strategy of most investigators has been to determine relative rate constants for competing channels by measuring the relative abundance of those end products that are believed to uniquely result from each of the paths. Reported rate constants vary greatly in both their certainty as well as their method of determination.[10] In some instances, rate constants are predicted on the basis of group additivity principles[12] and other thermodynamic arguments,[9,13,14] or are inferred empirically from

---

[†] Department of Environmental Engineering Science.

[‡] Department of Chemical Engineering.

[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1997.

S1089-5639(97)00212-0 CCC: \$14.00

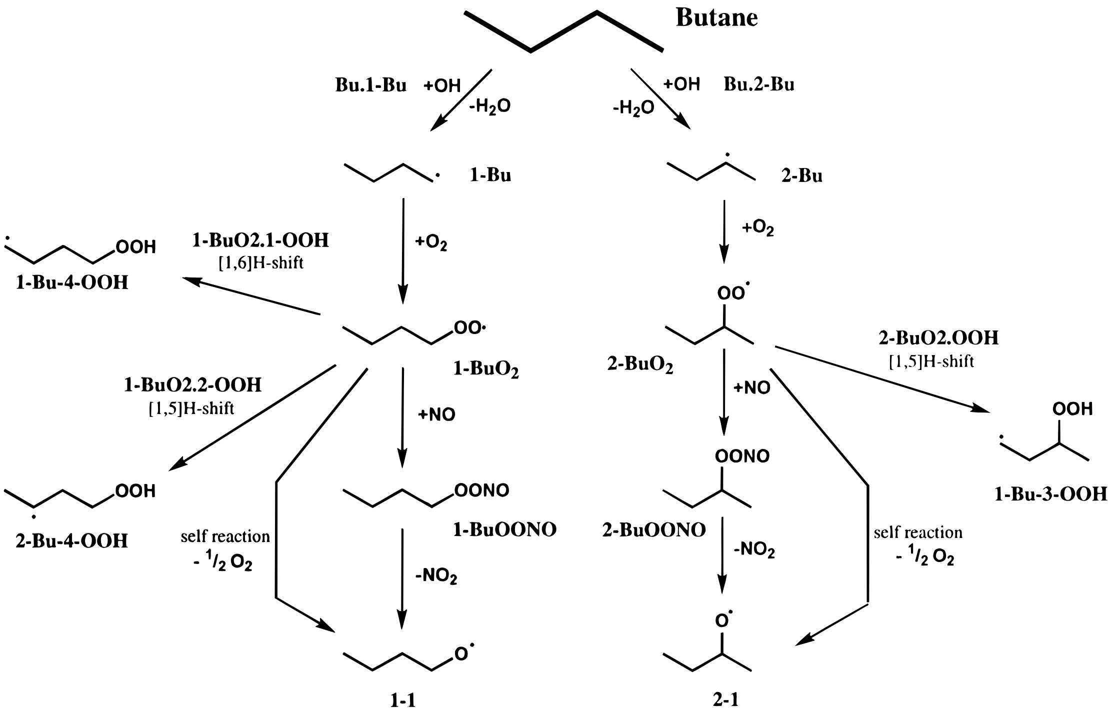

Figure 1. Chemical mechanism of initial steps in atmospheric *n*-butane oxidation.

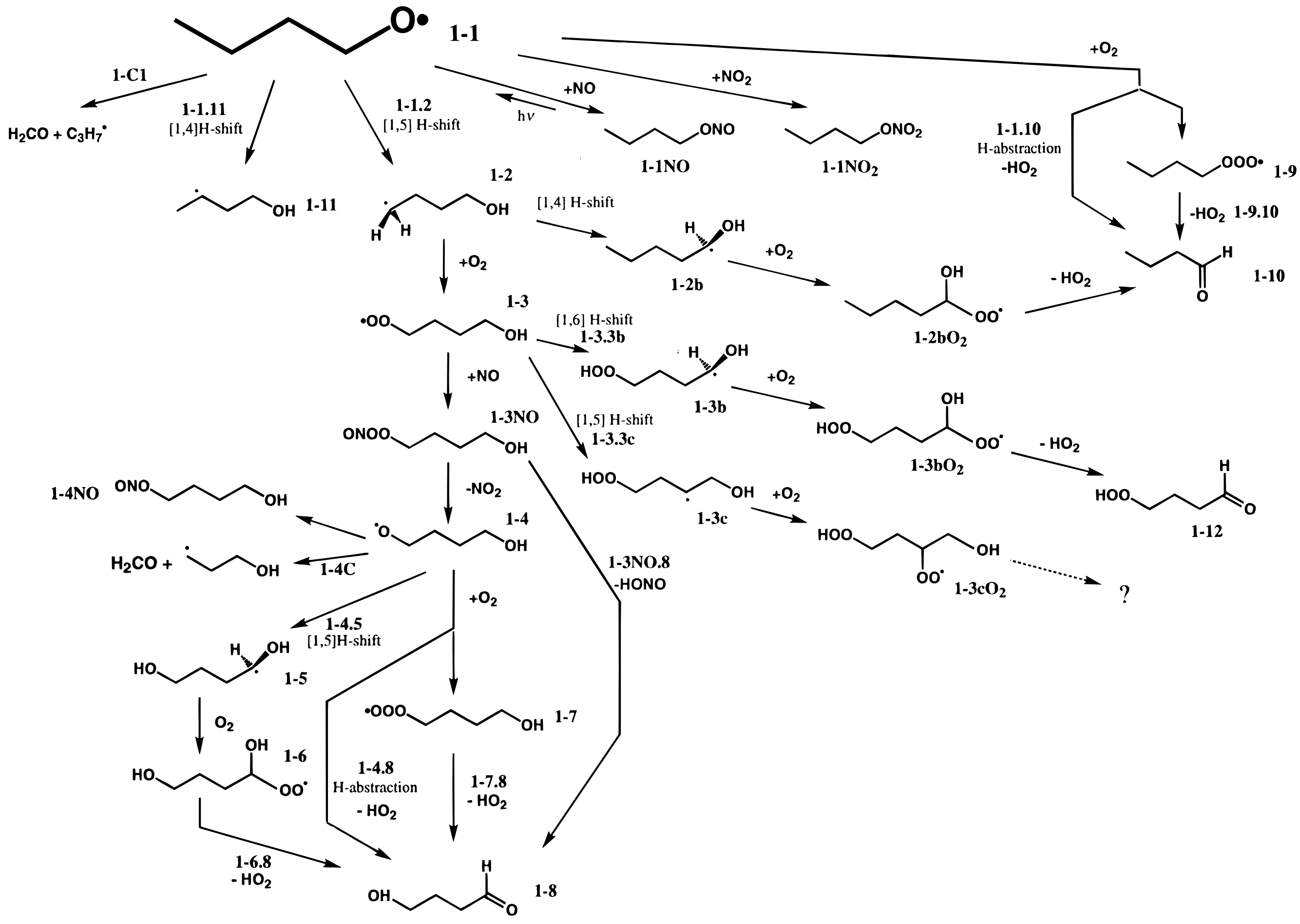

Figure 2. Reaction pathways of 1-butoxy radicals and subsequent steps.

behavior of similar species.[9] In other cases, the rates were calculated from the rate of disappearance of a specific reactant by assuming a product distribution.[15] Recently, the prediction of alkoxy radical rate constants was accomplished on the basis of observed systematic trends in reactivity with chain length.[10]

One problem with the approach of determining branching ratios by measuring product formation as described above is that observed products might not be solely linked to one of the three channels. For example, the formation of 1-butyraldehyde, commonly believed to result from the O_2 reaction channel of

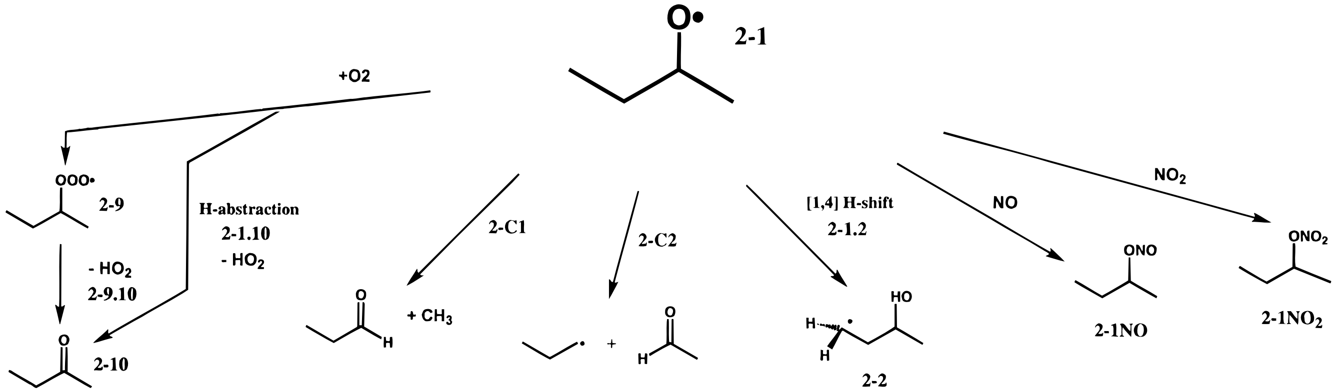

Figure 3. Reaction pathways of 2-butoxy radicals.

1-butoxy radicals, was found by Heiss *et al.*[3] to be independent of the O_2 concentration. Reinterpretation of data reported by Niki,[8] where previously O_2 dependence was concluded, seems to support the independence.[3] Similarly, HO_2 formation, which is linked to 1-butyraldehyde formation, is also found in the time dependent study of Mörs *et al.*[2] to be independent of O_2 concentration and to be formed early in the reaction mechanism. This indicates that the unimolecular isomerization channel possibly contributes to formation of 1-butyraldehyde. Also, C_3 fragments, usually regarded as representing the β-scission channel, can be formed by decomposition of alkoxy radical isomers formed after 1,5-H shift. In this way, the isomerization channel contributes to the yield of C_3 fragments.

To date relatively few theoretical studies exist on molecular properties and reactions of alkoxy radicals,[16−21] and only one set of *ab initio* calculations on isomerization of 1-butoxy radicals, also referred to as the Barton reaction,[22] exists while recent advances in tools for computational chemistry have allowed for accurate determination of stability and reactivity of a wide variety of compounds, calculations for species with more than four heavy atoms still represent a major challenge. Most studies in this class of compounds have focused on the methoxy radical,[16−19] since its small size allows the implementation of accurate, high-level calculations. Recently, computational techniques have been applied to methoxy reactions in an attempt to understand the mechanism by which alkoxy radicals react with O_2.[16,17] The application of computational techniques to the reactions of butoxy radicals can be particularly advantageous to completely determine the structure and stability of reaction intermediates. Such a study must address difficulties in calculation of absolute energies and especially activation energies for transition states (TS) with molecules containing up to eight heavy atoms.

2. Computational Aspects

2.1. Methodology. All calculations were performed using the parallel version of the GAUSSIAN94/LINDA program package[23] on a cluster of eight IBM RS/6000 workstations and on a 7-node IBM SP/2 parallel computer. Density functional theory geometry optimizations and frequency calculations for the species in this study were performed using the Becke3LYP hybrid functional as implemented in GAUSSIAN94.

Geometries were preoptimized and checked for conformational isomers using PM3, followed by optimization at the HF/3-21G and finally the B3LYP/6-31G(d,p) level of theory with tightened convergence cutoffs. Initial guesses at HF/3-21G for transition state geometries were successfully localized in many cases by synchronous transit-guided quasi-Newton methods (STQN) or constrained optimizations that were stepwise relaxed to full degree of freedom. Final transition state geometry optimizations at the B3LYP/6-31G(d,p) level were performed using either redundant internal coordinate schemes or eigenvalue following routines, both with analytical second-order gradients that were essential for locating the saddle points. Zero-point vibrational energies (ZPE) obtained at B3LYP/6-31G(d,p) were scaled with a factor of 0.9828 derived from experimental ZPE values for the molecules of the G1 set.[24]

The CBS-4 and CBS-q calculations[25] were performed using geometries and scaled ZPEs at the B3LYP/6-31G(d,p) level of theory, which replaced the HF/3-21G optimization and frequency calculation in the original formalism. The validity for this method modification is presented elsewhere and is shown to be able to predict activation energies for transition states with high accuracy.[24]

Energetic profiles for the reactions are discussed at two levels of theory: B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p) and CBS-q//B3LYP/6-31G(d,p), hereafter referred to concisely as B3LYP and CBS-q, respectively. The B3LYP level serves as reference for consistency, as do results obtained with B3LYP/6-31G(d,p)//B3LYP/6-31(d,p) and CBS-4//B3LYP/6-31G(d,p) calculations.

2.2. Reliablility of Energy Calculations. From the listing of 0 K reaction enthalpies ΔH_r and 0 K activation energies ΔE_0 for all 42 reactions considered in this work (Table 1) it can be seen that the two sets of B3LYP and CBS results are self-consistent with the exception of CBS values for reactions involving HO_2, *vide infra*. For discussion of chemical mechanisms in section 3, we will refer to the more reliable CBS-q and B3LYP/6-311+G(3df,2p) calculations only.

2.2.1. Enthalpies of Reaction. Good agreement is found comparing ΔH_r at the CBS-q level with values obtained with enthalpies of formation ΔH_f estimated using group additivity (GA) rules.[31] Expected deviation of ΔH_r occurs for cases involving trioxy radicals at the CBS level of theory. GA significantly overestimates ΔH_f of trioxy radicals.[16,17] While the energy of 1-butoxy **1-1** agrees well with the GA estimate, the energy of 2-butoxy **2-1** is found considerably higher at CBS levels of theory, causing the systematic deviations of ΔH_r values of reactions involving **2-1**. This bias also reduces barrier heights for these reactions, so these values are expected to be underestimated at CBS levels of theory.

Besides this exception, ΔH_r values at the CBS level seem to be more reliable than the DFT results. Large deviations of ΔH_r at the B3LYP level occur when the species $O_2(^3\Sigma_g)$ or NO_2 are involved, since the calculated atomization energies at B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p) of these two species are 3.5 and 6.2 kcal/mol, respectively, higher than the experimental values.

2.2.2. Barrier Heights. Considerable systematic disagreement among CBS values of activation energies occurs only for TS involving reaction with O_2 and formation of HO_2. These are non-isogyric reactions exhibiting excessive spin contamina-

TABLE 1: Reaction Enthalpies ΔH_r and 0 K Activation Energies ΔE_0 (kcal/mol) at Various Levels of Theory along with Group Additivity (GA)[31] Estimates of ΔH_r; Values Are Based on Geometries and ZPE Obtained at the B3LYP/6-31G(d,p) Level of Theory; B3LYP/big Refers to the 6-311+G(3df,2p) Basis Set, B3LYP/small to the 6-31G(d,p) Basis

			ΔE_0				ΔH_r				
reactants	TS	products	B3LYP/ big	B3LYP/ small	CBS-4	CBS-q	B3LYP/ big	B3LYP/ small	CBS-4	CBS-q	GA estimate
butane + OH	**Bu.1-Bu**	**1-Bu** + H_2O	−2.0[a]	−1.5[a]	2.5	1.4	−17.6	−12.2	−17.4	−16.8	*−17.8*
butane + OH	**Bu.2-Bu**	**2-Bu** + H_2O	N/A[b]	N/A	N/A	N/A	−21.6	−16.4	−20.7	−20.2	*−21.3*
1-Bu + O_2		**1-BuO$_2$**					−29.0	−30.7	−31.1	−34.4	*−33.0*
2-Bu + O_2		**2-BuO$_2$**					−29.2	−30.9	−33.1	−36.4	*−33.9*
1-BuO$_2$ + NO		**1-BuOONO**					−19.4	−21.0	−24.7	−21.5	*N/A*
2-BuO$_2$ + NO		**2-BuOONO**					−18.4	−21.1	−22.9	−21.9	*N/A*
1-BuO$_2$ + NO		**1-1** + NO_2					−16.3	−13.9	−10.1	−10.0	*−13.9*
2-BuO$_2$ + NO		**2-1** + NO_2					−14.1	−12.6	−7.3	−6.9	*−13.1*
1-BuO$_2$	**1-BuO$_2$.1-OOH**	**1-Bu-4-OOH**	24.6	25.0	23.3	25.4	19.1	22.1	17.5	20.3	*14.3*
1-BuO$_2$	**1-BuO$_2$.2-OOH**	**2-Bu-4-OOH**	21.3	21.9	18.9	20.3	14.6	16.9	12.8	15.5	*10.9*
2-BuO$_2$	**2-BuO$_2$.OOH**	**1-Bu-3-OOH**	23.9	24.8	22.8	24.3	19.2	21.8	17.0	19.7	*14.3*
1-1 + NO		**1-1NO**					−34.4	−37.4	−42.3	−41.9	*−41.9*
1-1 + NO_2		**1-1NO$_2$**					−35.5	−38.1	−47.3	−46.5	*−41.5*
1-1 + O_2	**1-1.10**	**1-10** + HO_2	8.2	7.9	12.0	27.5	−28.5	−24.2	−32.7	−35.7	*−33.0*
1-1 + O_2		**1-9**					7.9	5.4	14.4	−0.2	*+14.7*
1-9	**1-9.10**	**1-10** + HO_2	−1.8	−0.6	−4.0	20.8					
1-1	**1-1.2**	**1-2**	9.4	9.7	4.1	4.3	−0.8	2.9	−6.0	−4.5	*−2.8*
1-1	**1-1.11**	**1-11**	17.8	18.4	13.2	12.9	−4.7	−1.2	−8.5	−7.0	*−6.2*
1-1	**1-C1**	$H_2CO + C_3H_7$	12.9	15.6	10.7	9.8	7.6	11.8	7.0	6.8	*11.9*
1-2 + O_2		**1-3**					−31.2	−32.8	−33.0	−36.4	*−33.0*
1-2	1-2.2b	**1-2b**	19.7	18.4	19.1	20.0	−7.2	−7.8	−7.0	−8.6	*−6.1*
1-3 + NO		**1-3NO**					−19.7	−16.9	−22.1	−21.9	
1-3 + NO		**1-4** + NO_2					−13.9	−11.7	−10.9	−10.7	*−13.9*
1-3	**1-3.3b**	**1-3b**	18.4	21.0	18.0	19.4	14.4	16.6	12.7	15.3	*8.2*
1-3	**1-3.3c**	**1-3c**	24.8	25.1	21.4	22.9	18.4	21.0	15.4	18.2	
1-3NO	**1-3NO.8**	**1-8**	35.9	35.8	38.2	35.1					
1-4 + O_2	**1-4.8**	**1.8** + HO_2	8.5	8.2	18.6	34.3	−29.5	−25.2	−30.7	−33.7	*−33.0*
1-4 + O_2		**1-7**					8.8	6.1	18.0	3.3	
1-7	**1-7.8**	**1-8** + HO_2	−2.5	−1.2	0.2	25.4					
1-4 + NO		**1-4NO**					−34.8	−37.6	−40.1	−39.5	*−41.9*
1-4	**1-4C**	$H_2CO + C_3H_6OH$	13.2	15.7	14.1	13.2	7.4	11.6	9.3	9.1	*11.9*
1-4	**1-4.5**	**1-5**	4.8	4.1	3.4	2.0	−9.4	−6.4	−11.6	−10.4	*−8.9*
1-5 + O_2		**1-6**					−27.5	−29.6	−31.9	−35.3	*−37.2*
1-6	**1-6.8**	**1-8** + HO_2	6.2	4.9	11.5	11.2					
2-1	**2-1.2**	**2-2**	19.4	20.6	15.7	15.4	−3.0	1.4	−9.6	−8.4	*−3.6*
2-1	**2-C1**	$CH_3 + C_2H_5CHO$	12.7	16.1	9.9	9.0	3.1	8.5	3.3	2.6	*7.8*
2-1	**2-C2**	$C_2H_5 + CH_3CHO$	8.5	11.8	6.4	5.5	0.2	5.6	1.9	1.3	*7.1*
2-1 + NO		**2-1NO**					−35.3	−37.7	−44.0	−43.9	*−42.7*
2-1 + NO_2		**2-1NO$_2$**					−34.3	−36.1	−46.5	−46.2	*−42.3*
2-1 + O_2	2-1.10	**2-10** + HO_2	5.6	5.6	4.4	20.2	−36.6	−31.8	−40.1	−43.5	*−37.0*
2-1 + O_2		**2-9**					4.5	6.7	7.1	2.7	*13.9*
2-9	**2-9.10**	**2-10** + HO_2	−3.5	−3.0	−9.9	9.4					

[a] Although the classical barrier height is positive, the activation energy including the ZPE at B3LYP levels of theory is calculated to be negative in the case of **Bu.1-Bu**. The negative value is a result of considerable decrease in ZPE in this type of TS compared to the reactants, since one high-energy C−H stretching mode is lost as a vibrational degree of freedom in the TS. [b] No saddle point on the potential energy surface.

tion in the UHF wave functions underlying the CBS components. The spin contamination causes slow convergence of the perturbation series expansion. The effect of spin contamination is treated quite effectively in CBS-q by the QCISD(T) component, where the leading spin contaminant is projected out. In CBS-4 the effect of spin contamination is treated by an empirical correction term based on the $\langle S^2 \rangle$ of the HF/CbsB1 wave function. The inaccuracy of this empirical correction for severe spin contamination leads to considerable underestimation of barrier heights.[24]

There exists another class of TS within our set of reactions where CBS-4 and CBS-q values are consistent among themselves, but still inconsistent with the DFT values. These TS comprise those isogyric reactions involving C−C bond cleavage that have spin-contaminated UHF wave functions. The degree of contamination for the C−C cleavage cases ($\langle S^2 \rangle$ around 0.9) is not as high as for the non-isogyric transition states discussed above, where $\langle S^2 \rangle$ values are found around 1.7 (*cf.* Table I in the Supporting Information). The lower spin contamination and therefore lower and more reliable empricial spin correction term in CBS-4 lead to CBS-4 and CBS-q values that are comparable. Still, they are noticeably different from the DFT values.

Since in the cases of reactions involving HO_2 the CBS-q values are higher than the DFT ones, and for C−C cleavage cases the CBS-q value is lower than the DFT values, it remains undecided in these troublesome cases whether the DFT or CBS value represents the more reliable estimate.

3. Results and Discussion

The conceptually possible reaction pathways of *n*-butane photooxidation indicated in Figures 1−3 represent the extent of calculations that were performed. The following description of the results uses the labeling scheme shown in these figures. Compounds labeled with the prefix **1-** are associated with the 1-butyl system, and **2-** for 2-butyl. The naming of the TS refers to the species that a particular TS connects, *e.g.,* **1-1.2** being the TS for the rearrangement of **1-1** into **1-2**. A list with schematic structures and names of nontrivial species involved is presented in Figure 4 along with the most important bond distances at the B3LYP/6-31G(d,p) level of theory.

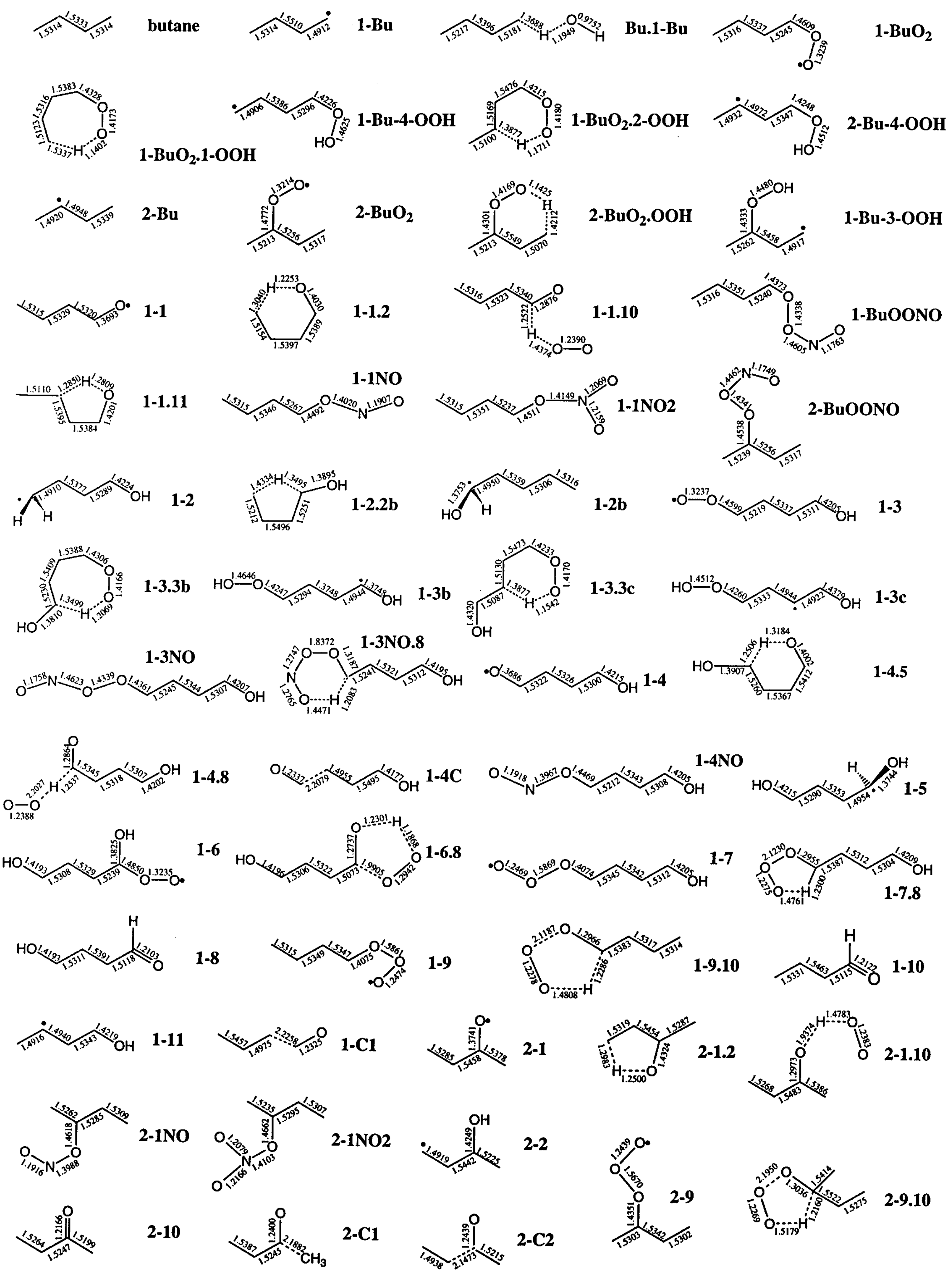

Figure 4. Structures and nomenclature of nontrivial species, bond lengths given in angstroms at the B3LYP/6-31G(d,p) level of theory.

When reporting energies without stating the level of theory explicitly, we refer to the CBS-q result, with the B3LYP value given in parentheses. The full set of absolute energies and components of CBS-4 and CBS-q calculations is given in the Supporting Information. The derived 0 K activation energies and enthalpies of reactions are presented in Table 1. Figures 4

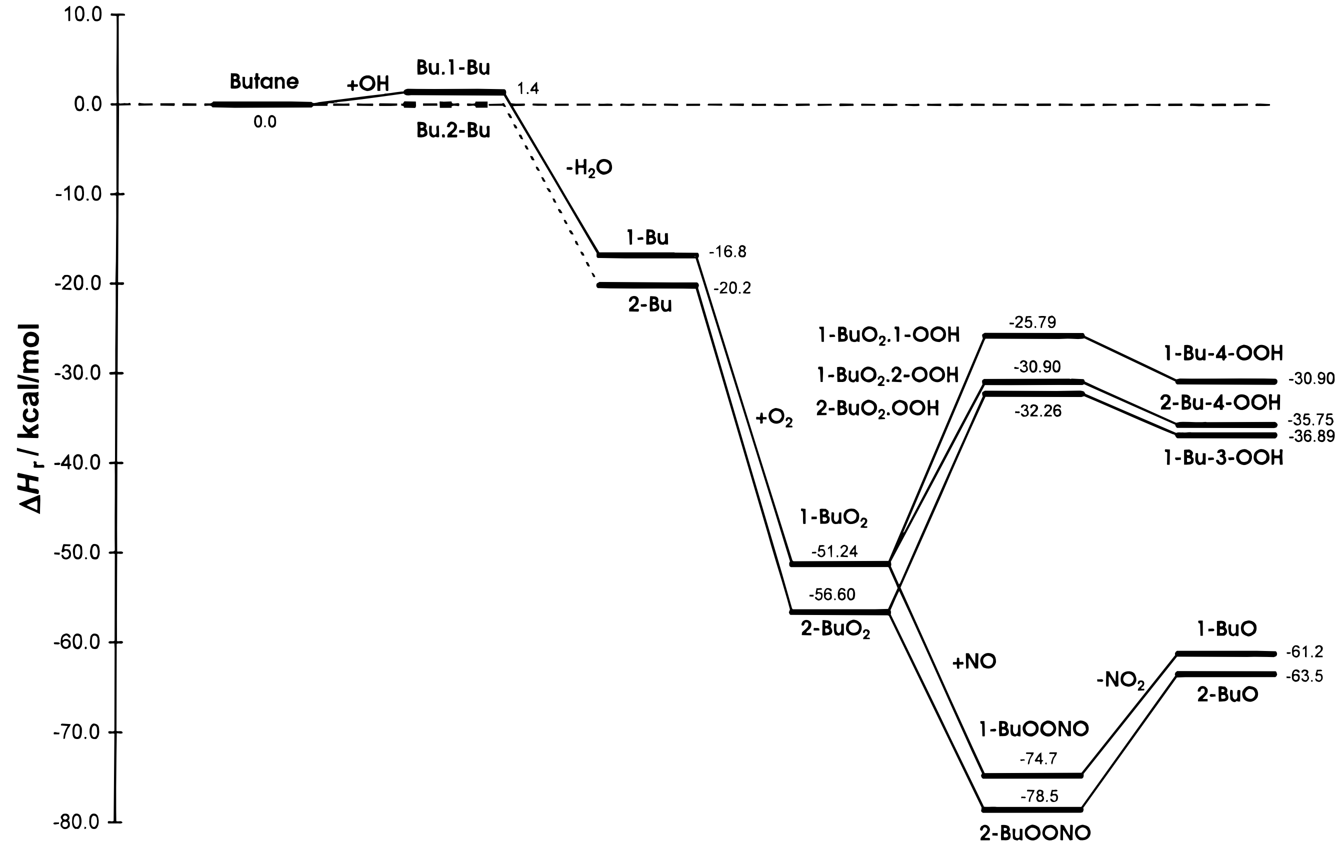

Figure 5. Energy profile of initial reaction steps of *n*-butane oxidation at the CBS-q//B3LYP/6-31(d,p) level of theory. Reaction enthalpies ΔH_r at 0 K for consecutive reaction steps are biased to ΔH_r of the previous step. Dashed line: barrier height of H abstraction not available; see text.

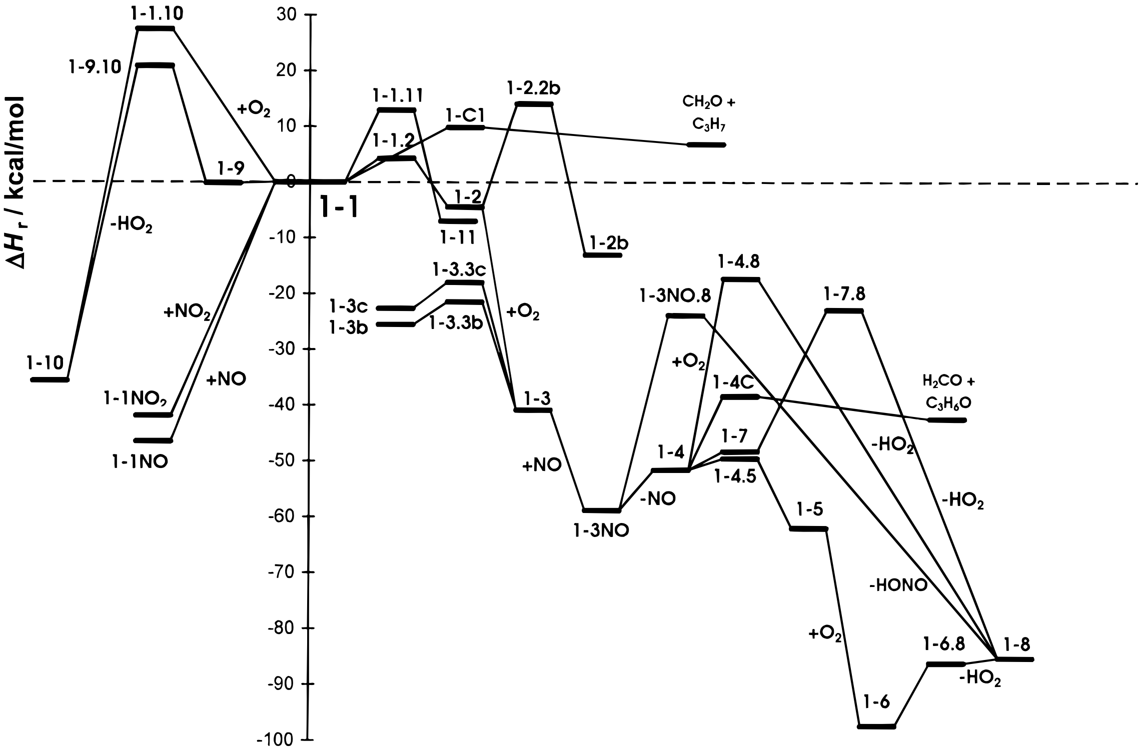

Figure 6. Energy profile of 1-butoxy reactions and subsequent steps at the CBS-q//B3LYP/6-31(d,p) level of theory. Reaction enthalpies ΔH_r at 0 K for consecutive reaction steps are biased to ΔH_r of the previous step.

through 6 are energy profiles constructed from the data in Table 1. Multiple reaction sequences are lumped into one figure in order to facilitate evaluation of the most likely pathways.

We investigated the oxidation pathway of *n*-butane starting with OH reaction, leading to the primary and secondary butyl radicals labeled **1-Bu** and **2-Bu**, respectively. Reaction with O_2 leads to formation of the peroxy radicals **1-BuO$_2$** and **2-BuO$_2$**, whose fate is determined by reaction with NO or unimolecular isomerization to hydroperoxy alkyl radicals, as indicated in Figure 1. After NO/NO_2 conversion, the 1-butoxy and 2-butoxy radicals labeled **1-1** and **2-1**, respectively, are obtained. Subsequent reactions of the two alkoxy radicals **1-1** and **2-1** are the major focus of this work. For both systems, all possible unimolecular decomposition/rearrangement channels and bimolecular reactions with O_2, NO, and NO_2 were investigated computationally. In the case of **1-1**, which apparently undergoes 1,5-H shift (*vide infra*), the fate of the resulting 4-hydroxy-1-butoxy radical **1-4** was investigated to the same extent. It can undergo the same reactions as **1-1**, including a second 1,5-H shift and subsequent reactions to stable products, and a 1,4-H shift that had been proposed.[3] The fate of **1-11** as a product of 1,4-H shift in **1-BuO** was not investigated, since it is deemed to be unlikely in the atmosphere because of the high barrier of 12.9 (17.8) kcal/mol. For the same reason the fate of **2-2**, which would also be the product of a 1,4-H shift, was not investigated beyond its formation pathway, which was found to have a barrier of 12.7 (19.4) kcal/mol.

3.1. Initial Butane Reactions: H Abstraction by OH. The initial OH attack on *n*-butane is found to have a very low barrier for the H abstraction transition state **Bu.1-Bu** leading to 1-butyl **1-Bu**. At the CBS-q level of theory, the activation energy is predicted to be 1.4 kcal/mol, which is very close to experimental values ranging from 0.5 to 1.8 kcal/mol.[9] The geometry for a saddle point for the secondary abstraction reaction TS **Bu.2-Bu** with formation of 2-butyl **2-Bu** could not be localized because of the very flat potential, even though an extensive search with analytical second-order gradients at the B3LYP/6-31G(d,p) level of theory was performed. The shallow potential for OH attack at both primary and secondary H atoms in *n*-butane is not unexpected, since the activation energy found experimentally for formation of 1-butyl is slightly positive (0.5−1.8 kcal/mol) and that of 2-butyl is slightly negative (−0.8 kcal/mol).[9]

3.2. Formation of Butyl Peroxy Radicals. Once **1-Bu** and **2-Bu** are formed, with **2-Bu** being lower in energy, as expected for a secondary alkyl radical, subsequent reaction with O_2 leads to formation of the peroxy radicals **1-BuO$_2$** and **2-BuO$_2$**. No barriers for these recombination reactions could be located. Since isomerization of the butyl peroxy radicals via 1,5-H shift is conceptually possible in both **1-BuO$_2$** and **2-BuO$_2$** as well as 1,6-H shift in **1-BuO$_2$** (Figure 1), we investigated the possibility of these reactions. They are found to be thermodynamically accessible by formation of the chemically activated butyl peroxy radicals and subsequent isomerization to the hydroperoxy butyl radicals (Figure 5). Enough energy is available for these processes to overcome the barriers for 1,5-H shifts in **1-BuO$_2$** and **2-BuO$_2$**, as well as the 1,6-H shift in **1-BuO$_2$**. Collisional stabilization will be the major process at atmospheric temperatures, as determined by QRRK calculation.[26] The estimate of the apparent rate constant of **4-OOH-2-Bu** formation in the reaction **1-Bu** + O_2 is 1.0×10^{-16} molcule cm^{-3} s^{-1} at atmospheric pressure and room temperature using enthalpies and entropies obtained at the CBS-q level of theory. Compared to 7.5×10^{-12} molecules cm^{-3} s^{-1} as the high pressure limit rate constant for the formation of **1-BuO$_2$**, these isomerization processes are considered to be of minor importance at ambient T and $[O_2]$.

3.3. Formation of Butoxy Radicals. NO/NO_2 conversion by reaction of **1-BuO$_2$** and **2-BuO$_2$** leads to formation of the alkoxy radicals **1-1** and **2-1**, respectively. The energy of **2-1** is predicted to be lower than **1-1** by 2.1 and 2.3 at the B3LYP and CBS-q level, respectively. These results indicate that the isomers **1-1** and **2-1** are essentially of equal energy within the error limit of the methods used. However, the energy of **2-1** seems to be overestimated by the CBS models, which leads to the differences between DFT and CBS reaction energies for **2-BuO$_2$** + NO → **2-1** + NO_2.

Formation of **1-1** and **1-2** involves the chemically activated species **1-BuOONO** and **2-BuOONO**. We investigated the case of CH_3OONO as a model species, but no isomerization TS leading to formation of CH_3ONO_2 could be located at the B3LYP/6-31G(d,p) level. Thus, no attempt to locate this three-centered transition state for the butyl species was made. At this point we assume the sole fate of the peroxy nitrite species **1-BuOONO** and **2-BuOONO**, besides collision deactivation and photolysis, to be decomposition into NO_2 plus **1-BuO** and **2-BuO**, respectively.

3.4. Fate of 1- and 2-Butoxy Radicals. Six reaction pathways are conceptually available for both **1-1** and **2-1**; see Figures 2 and 3. Three of these are bimolecular reactions with species present in ambient air, *i.e.* O_2, NO, and NO_2; the remaining channels are unimolecular reactions of each alkoxy radical.

3.4.1. Reaction with O_2. The reaction of alkoxy radicals with O_2 is traditionally assumed to proceed via H abstraction, forming HO_2 and the corresponding aldehyde. Only most recently have the intrinsic difficulties imposed on the quantum chemical treatment of this system been revealed.[17] It was demonstrated that the H abstraction channel cannot contribute to aldehyde formation at room temperature.[16] The reaction proceeds via trioxy intermediates with subsequent rearrangement via a five-membered TS leading to HO_2 and the aldehyde. The level of theory needed to produce a reliable description of the energetics, however, was very high (G2M(RCC) and CBS-QCI/APNO were used) and clearly cannot be used for the calculation with seven heavy atoms involved in the butoxy reaction. However, the level of theory employed here is at least qualitatively capable of reproducing the energetic profile of the alkoxy radical mechanism (Figure 6). It is apparent that the H abstraction mechanism described by TS **1-1.10** has a barrier that is found consistently higher by 6.7 (10) kcal/mol than that encountered within the alternative pathway. This involves the formation of the trioxy radical **1-9** and subsequent HO_2 elimination via the five-membered TS **1-9.10** that is low compared to **1-1.10**.

3.4.2. Reaction with NO and NO_2. The remaining bimolecular reaction channels of the reactions of **1-1** and **2-1** with NO and NO_2 have been calculated, with heats of reaction given in Table 1. The energy of 1-butyl nitrate **1-1NO$_2$** is found lower than that of its isomer 1-butyl peroxy nitrite **1-BuOONO** by 34.9 (33.2) kcal/mol. A similar difference of 31.1 (29.9) kcal/mol is found for the 2-butyl system.

3.4.3. β-Scission. The only possible β-scission process in **1-1** is found to be endothermic by 6.8 (7.6) kcal/mol, as expected from thermochemical estimates. The barrier though is found to be as low as 9.8 (12.9) kcal/mol and seems to occur very late ($r_{C1-C2} = 2.23$ Å), resembling the geometry of the products quite closely. The cleavage of the C_1-C_2 bond in **2-1** is found nearly thermoneutral ($\Delta H_r = -1.3$ (+0.1) kcal/mol, but has to overcome TS **2-C1** ($r_{C1-C2} = 2.18$ Å) with a barrier of 6.4 (12.6) kcal/mol (Figure 7). The profile of the C_2-C_3 bond cleavage in **2-1** is a little less exothermic ($\Delta H_r = 0.0$ (+3.0) kcal/mol) but requires less activation energy for TS **2-C2** (2.8 (8.5) kcal/mol, $r_{C1-C2} = 2.14$ Å), indicating that this β-scission leading to C_2H_5 radicals and CH_3CHO represents a major degradation pathway at room temperature. The barrier heights found for the two possible β-scission processes in **2-1** are considerably lower than the values derived from experimental data of 16.6 kcal/mol for **2-C1** and 14.3−15 kcal/mol for **2-C2**.[4,10] There exists no absolute experimental measure of these barrier heights, since they are derived from the temperature dependence of rates of C_3 product formation relative to the rate of **2-1** + NO[10] or the rate of product formation assigned to **2-1** + O_2.[4] If the

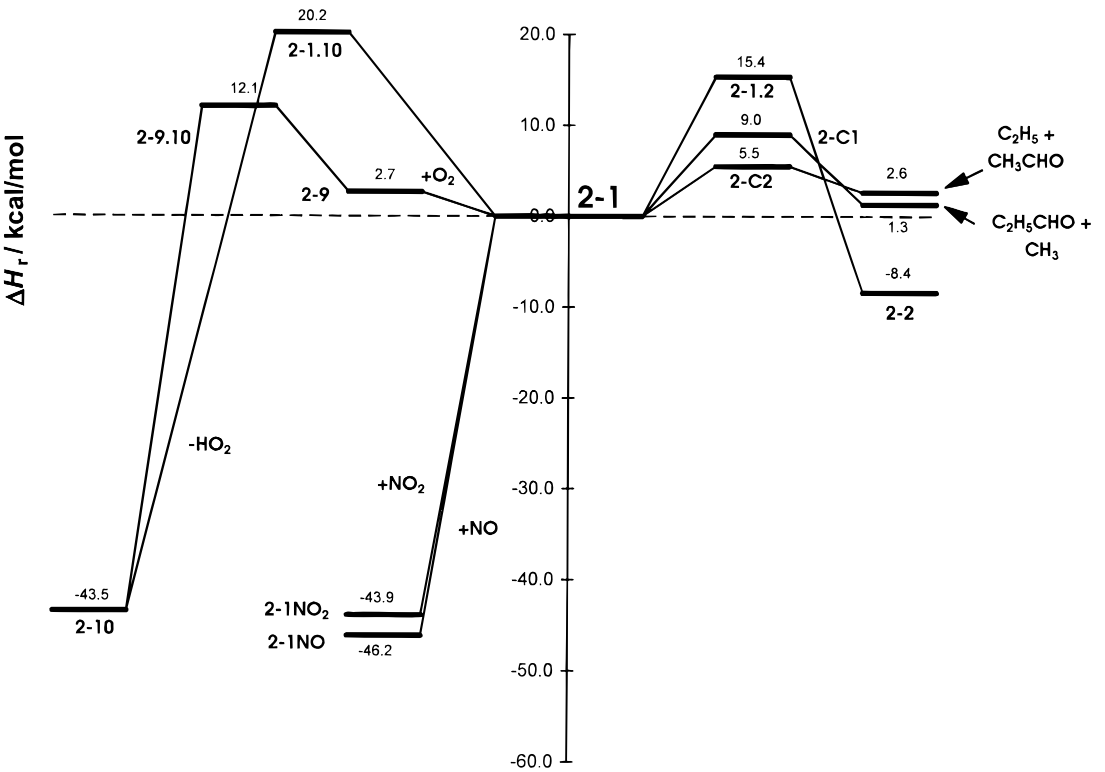

Figure 7. Energy profile of 2-butoxy reactions at the CBS-q//B3LYP/6-31(d,p) level of theory. Reaction enthalpies ΔH_r at 0 K for consecutive reaction steps are biased to ΔH_r of the previous step.

measured product concentrations are not uniquely linked to these particular reaction channels, the derived activation energy is directly affected by uncertainties in rates and activation energies of these reference reactions.

3.4.4. 1,5-H and 1,4-H Shift. The six-membered TS **1-1.2** for 1,5-H shift in 1-butoxy is found to have a fairly low barrier of 4.1 (9.4) kcal/mol, while the exothermicity of the reaction **1-1** → **1-2** is not very pronounced ($\Delta H_r = -4.5$ (-0.8) kcal/mol). The DFT value of the activation energy is close to that of 9.7−10.7 kcal/mol recently reported by Heiss *et al.*[3] On the other hand, the TS **1-1.11** for the 1,4-H shift in **1-1** has a comparably high barrier of 12.9 (17.8) kcal/mol, and therefore this channel seems not to be accessible at atmospheric temperatures. The same finding holds for the 1,4-H shift in **2-1**, which also seems to be a negligible channel with a barrier of 12.7 (19.3) kcal/mol. This shows that a minimum of TS ring size of six is needed for intramolecular H abstraction to be important and that, in accord with experimental results, in fact butane is the smallest alkoxy radical precursor where the H shift has impact on the oxidation pathway.

The isomerization of alkoxy radicals via 1,5-H shift has always been inferred from experimental results, but theoretical work is scarce.[21,22] The 298 K activation enthalpy by Houk *et al.* of 11.0 kcal/mol for the 1,5-H shift was derived at the MP2/6-31G(d)//HF/3-21G level.[22] Recent predictions based on BAC-MP4 activation energies for alkyl radical isomerization of 25.1 and 18.8 kcal/mol for 1,4-H and 1,5-H shift, respectively, have been published but seem to be high with respect to the accepted values of 12−21.5 and 12 kcal, respectively.[27] Our 1,4-H shift data for **1-1.11**, **1-2.2b**, and **2-1.2** of consistently 20 (DFT) and 12−20 kcal/mol (CBS-q) fall into that given range. Our DFT and CBS-q values for both 1,5-H shifts involving butoxy radicals, *i.e.*, **1-1.2** and **1-4.5**, are relatively low, even lower than the MP2 value for 1,5-H shift by Houk *et al.*

3.4.5. Rate Constant Calculations. With molecular parameters and energy barriers in hand, we were able to calculate unimolecular rate constants for the decomposition processes of **1-1** and **2-1** on the basis of RRKM theory. Density of states and microscopic rate coefficients, $k(E)$, were calculated using the UNIMOL suite of programs.[28] Due to the presence of tight transition states, momentum conservation was treated only in the high-pressure limit. All internal rotations were treated as low-frequency torsional modes. External rotations were considered inactive for the isomerization pathways of **1-1**. For the case of **2-1**, species were modeled as symmetric tops with one active rotational degree of freedom, as is common for dissociation reactions. Collisional energy transfer leading to the derivation of $k(T,p)$ was computed using a simple strong collision assumption. Buffer gas was treated as N_2.

The uncertainty in activation energy calculation leads to a range of rate constants that spans several orders of magnitude when either the CBS-q or B3LYP values are used (B3LYP energy based rate constants given in parentheses): the 1,4- and 1,5-H shifts in 1-butoxy **1-1** have high pressure limit rate constants $k^{\infty}_{1,4-\mathrm{H}} = 10^{12.25} \exp(-(12.9\ \mathrm{kcal/mol})/RT)\ \mathrm{s}^{-1}$ and $k^{\infty}_{1,5-\mathrm{H}} = 10^{11.73} \exp(-(4.3\ \mathrm{kcal/mol})/RT)\ \mathrm{s}^{-1}$, respectively. The 1,5-H shift is calculated by RRKM theory with a rate of $k_{1,5-\mathrm{H}} = 3.7 \times 10^8$ (1.3×10^5) s^{-1} at $T = 298$ K and $p = 1$ atm, whereas the 1,4-H shift with $k_{1,4-\mathrm{H}} = 1.9 \times 10^2$ (1.6×10^{-1}) s^{-1} is slower by 2×10^6 (4×10^6). The B3LYP result for the 1,5-H shift is very close to the recent value of Heiss *et al.*[3] ($9.9 \times 10^4\ \mathrm{s}^{-1}$) and the recommendation of Atkinson[10] ($1.6 \times 10^5\ \mathrm{s}^{-1}$).

For 2-butoxy **2-1** the high pressure limit rate expressions for the two β-scission processes are $k^{\infty}_{2-\mathrm{C1}} = 10^{14.01} \exp(-(9.0\ \mathrm{kcal/mol})/RT)\ \mathrm{s}^{-1}$ and $k^{\infty}_{2-\mathrm{C2}} = 10^{14.03} \exp(-(5.5\ \mathrm{kcal/mol})/RT)\ \mathrm{s}^{-1}$. At $T = 298$ K and 1 atm the apparent rates obtained by RRKM theory are $k_{2-\mathrm{C1}} = 2.14 \times 10^5$ (1.7×10^3) s^{-1} and $k_{2-\mathrm{C1}} = 3.90 \times 10^8$ (8.3×10^6) s^{-1}. These rates are considerably higher than those derived by Atkinson[10] for the $CH_3 + C_2H_5CHO$ cleavage ($k_{2-\mathrm{C1}} = 10^{14.3} \exp(-(16.6\ \mathrm{kcal/mol})/RT)\ \mathrm{s}^{-1} = 1.3 \times 10^2$ at $T = 298$ K) and $C_2H_5 + CH_3CHO$ cleavage (values for $k_{2-\mathrm{C2}}$ from $= 10^{14.3} \exp(-(14.3\ \mathrm{kcal/mol})/RT)\ \mathrm{s}^{-1} = 6.5 \times 10^3\ \mathrm{s}^{-1}$ at $T = 298$ K up to $2.5 \times 10^4\ \mathrm{s}^{-1}$). The pre-exponential factor log $A = 14.03$ for reaction **2-1** → $C_2H_5 + C_2H_5CHO$ via TS **2-C1** is within the range 13.8−14.3 derived from experimental data[4,10] and matches the earlier thermochemical estimate of 14.08 by Heiss *et al.*[4] The deviations for the rate constants of β-scission processes in **2-1** are caused by a bias in barrier heights that arise from an overestimated enthalpy of **2-1** at the CBS-q level compared to the DFT values; see paragraph 2.2.1.

3.5. Fate of 4-Hydroxy-1-butyl Radicals. Once the rearrangement of **1-1** into **1-2** occurs, the entire chain of reactions that apply to the 1-butyl radical will apply again to the 4-hydroxy-1-butyl radical **1-2**, *i.e.*, bimolecular reaction with O_2 and NO as well as each of the three bimolecular and unimolecular decomposition channels open to the resulting 4-hydroxy-1-butoxy radical **1-4**. These include yet another 1,5-H shift leading to the 1,4-dihydroxy-1-butyl radical **1-5**, which, after reaction with O_2 and HO_2 elimination, forms the 4-hydroxy-1-butanal **1-8**. HO_2 elimination from the 1-hydroxy-1-peroxy radical **1-6** that is formed as a chemically activated species is found to proceed via a very flat potential barrier, leading to the aldehyde **1-8**. This step is the reverse reaction corresponding to that of formaldehyde with HO_2, which is known to proceed via a five-membered transition state that was actually calculated to be lower in energy than $HO_2 + CH_2O$.[29] This indicates formation of a loose complex, which also has been implied from fitting experimental data to a kinetic model of the system $CH_2OH + O_2$.[30]

Other channels conceptually possible forming **1-8** seem to be minor on the basis of activation energies for these processes, including the reaction of **1-4** with O_2, which would directly lead to formation of the aldehyde **1-8**. Contributing to further complexity are channels like HONO elimination from **1-3NO**, but this pathway will not contribute to **1-8** formation at low temperatures, since the barrier is far too high. The proposed formation of 1-butanal **1-10** by isomerization of **1-2** by 1,4-H shift leading to 1-hydroxy-1-butyl-radicals **1-2b** and subsequent O_2 addition and HO_2 elimination was also investigated to the point of formation of the isomerized alkyl radical **1-2b** via transition state **1-2.2b**. It is concluded that this pathway will not contribute to formation of **1-10** when O_2 is present, since addition with O_2 is expected to be very fast and the concentration of **1-2** in the equilibrium **1-2** + $O_2 \Leftrightarrow$ **1-3** will be depleted by the subsequent reactions of **1-3**. Thus with low stationary concentrations of **1-2**, this reaction is not expected to explain the amount of **1-10** that is found experimentally to be formed independent of O_2 concentration in the degradation pathway of **1-1**.

Furthermore the O_2 independent prompt HO_2 formation observed by Zellner *et al.*[2] is also most probably not related to this 1,4-H shift. Fast HO_2 formation could, however, be explained by unimolecular isomerization of the peroxy radical **1-3** with formation of 4-hydroperoxy-1-hydroxy **1-3b**. In contrast to the reaction of **1-Bu** + O_2, the 1,6-H shift is energetically lower that the 1,5-H shift, leading to **1-3c**. Similar to the reaction **1-Bu** + O_2, **1-3** is formed chemically activated in the reaction **1-2** + O_2 and can undergo isomerization via TS **1-3.3b** to **1-3b** or **1-3.3c** to **1-3c**, respectively. TS **1-3.3b** was found to be lower in energy than TS **1-3.3c** by 4.4 (6.0) kcal/mol, so formation of **1-3b** will dominate and subsequent reaction steps of O_2 addition and HO_2 elimination lead to 4-hydroperoxy-1-butanal. Recently, the experimental limits of the GC/MS detection were overcome by Heiss and Sahetchian by using CI-MS/MS and micropreparative GC/NMR,[11] proving formation of the hydroperoxide **1-12** as a product of the oxidation of 1-butoxy radicals. Formation of **1-12** can be rationalized by the pathway via **1-3b** and should be dependent on the NO concentration, since isomerization of **1-3** to **1-3b** competes with NO reaction and formation of **1-4**. The activation energy of 19.4 (18.4) kcal/mol for isomerization of **1-3** is close to the value of 17.6 kcal/mol derived experimentally.[11] No energy calculations of the subsequent O_2 addition and HO_2 elimination steps for **1-3b** or **1-3c** were performed, since the treatment of species with nine and more heavy atoms was beyond the available resources. The energetics in terms of released bond energy for O_2 addition and barrier for HO_2 elimination are assumed to be similar to those calculated for the reactions of **1-5** → **1-6** → **1.8**, the analogous pathway with the hydroxy group in the δ-position instead of the hydroperoxy function in **1-3b**.

4. Atmospheric Implication

The major features of the atmospheric *n*-butane oxidation mechanism and relative importance of competing reaction channels have been predicted theoretically. The key role of 1- and 2-butoxy radicals on the expected product distribution is confirmed. The fate of 1-butoxy, also serving as a model species for alkoxy radicals derived from larger alkanes, is found to be isomerization via 1,5-H shift. This process was calculated to have a sufficiently low barrier to be important at atmospheric temperatures and clearly dominates over β-scission, which in addition to having a higher barrier height would be endothermic. Subsequent steps of hydroxybutyraldehyde formation including a further 1,5-H shift were calculated and found to be a major product channel. Formation of hydroperoxy compounds by isomerization of chemically activated butyl peroxy radicals **1-BuO$_2$** and **2-BuO$_2$** as well as 4-hydroxy-1-butyl peroxy radical **1-3** is found to be energetically possible. The barriers for isomerization of **1-BuO$_2$** and **2-BuO$_2$** are too high to be important at ambient temperature. However in the case of **1-3**, the lower barrier for peroxy isomerization could make the pathway of hydroperoxide formation important at ambient temperatures and NO_x levels.

The only reaction channel of 2-butoxy radicals of major atmospheric importance besides the competing bimolecular reaction with O_2 is β-scission, with formation of the C_2 alkyl radical favored over formation of the C_1 alkyl radical, in accord with experimental findings. 1,4-H shift can be ruled out for both 1- and 2-butoxy radicals as an important pathway because of the high activation energies calculated for the isomerization. The reaction mechanism of both 1- and 2-butoxy radicals with oxygen is found not to occur via H abstraction but rather an addition/elimination mechanism involving trioxy radical species.

Quantitative information that is needed for further kinetic modeling by RRKM or QRRK formalisms is obtained in this work at the CBS-q//B3LYP/6-31G(d,p) level of theory based on DFT geometry optimizations. Whereas reaction enthalpies are expected to have chemical accuracy, deviations in absolute values of activation energies are still a major source of error when calculating rate constants for unimolecular decomposition reactions, as demonstrated for the decomposition rates of 1- and 2-butoxy radicals. It is expected that oxidation mechanisms of larger alkanes, where even higher complexity with increasing number of possible reaction channels is expected, can be modeled on the basis of properties like energies and activation energies found for the butane system.

Acknowledgment. T.P.W.J. gratefully acknowledges a "Forschungsstipendium der Deutschen Forschungsgemeinschaft". Generous allocation of CPU time on the IBM SP/2 by the Center for Advanced Computing Research (CACR) at the California Institute of Technology is acknowledged. We are obliged to Anthony M. Dean of Exxon Research and Engineering Company for providing us with the program CHEMACT. We thank Mr. Kiran Shekar for performing numerous GAUSS-

IAN94 calculations and Mr. Bryan Hathorn for his assistance on RRKM theory. This research was supported in part by U.S. Environmental Protection Agency Center on Airborne Organics R-819714-01-0.

Supporting Information Available: Tables with absolute energies at B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), CBS-4//B3LYP-6-31G(d,p), and CBS-q//B3LYP-6-31G(d,p) levels of theory and the components of the CBS-4 and CBS-q calculations as well as rotational constants and calculated vibrational frequencies of all species are available (12 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Kwok, E. S. C.; Arey, J.; Atkinson, R. *J. Phys. Chem*. **1996**, *100*, 214.

(2) Mörs, V.; Hoffmann, A.; Malms, W. Zellner, R. *Air Pollut. Res. Rep*. **1996** *57*, 273.

(3) Heiss, A.; Sahetchian, K. *Int. J. Chem. Kinet*. **1996**, *28*, 531.

(4) Heiss, A.; Tardieu de Maleissye, J.; Viossat, V.; Sahetchian, K., Pitt, I. G. *Int. J. Chem. Kinet*. **1991**, *23*, 607.

(5) Morabito, P.; Heiklen, J. *J. Chem. Soc. Jpn.* **1987**, *60*, 2641.

(6) Drew, R. M.; Kerr, J. A.; Olive, J. *Int. J. Chem. Kinet*. **1985**, *17*, 167.

(7) Cox, R. A.; Patrick, K. F.; Chant, S. A. *Environ. Sci. Technol*. **1981**, *15*, 587.

(8) Niki, H.; Maker, P. D.; Savage, C. M.; Breitenbach, L. P. *J. Phys. Chem*. **1981**, *85*, 2698.

(9) Atkinson, R. *J. Phys. Chem. Ref. Data Monogr*. **1994**, *2*, 1.

(10) Atkinson, R. *Int. J. Chem. Kinet*. **1997**, *29*, 99.

(11) Jorand, F.; Heiss, A.; Sahetchian, K.; Kerhoas, L.; Einhorn, J. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 4167.

(12) Choo, K. Y.; Benson, S. W. *Int. J. Chem. Kinet*. **1981**, *13*, 833.

(13) Balla, R. J.; Nelson, H. H.; McDonald, J. R. *Chem. Phys*. **1985**, *99*, 133.

(14) Baldwin, A. C.; Barker, J. R.; Golden, D. M.; Hendry, D. G. *J. Phys. Chem*. **1977**, *81*, 2483.

(15) Atkinson, R.; Kwok, E. S. C.; Arey, J.; Aschmann, S. M. *Faraday Discuss*. **1995**, *100*, 23.

(16) Jungkamp, T. P. W.; Seinfeld, J. H. *Chem. Phys. Lett.* **1996**, *263*, 371.

(17) Jungkamp, T. P. W.; Seinfeld, J. H. *Chem. Phys. Lett.* **1996**, *257*, 15.

(18) Taketsugu, T.; Tajima, N.; Hirao, K. *J. Chem. Phys.* **1996**, *105*, 1933. Schneider, W. F.; Nance, B. I.; Wallington,T. J. *J. Am. Chem. Soc.* **1995**, *117*, 478. Bent, G. D. *J. Chem. Phys.* **1994**, *100*, 8219. Tachikawa, H. *Chem. Phys. Lett*. **1993**, *212*, 27. Glauser, W. A.; Koszykowski, M. L. *J. Phys. Chem.* **1991**, *95*, 10705. Curtiss, L. A.; Kock, L. D.; Pople, J. A. *J. Chem. Phys.* **1991**, *95*, 4040. Bent, G. D.; Adams, G. F.; Bartram, R. H.; Purvis, G. D.; Bartlett, G. D. *J. Chem. Phys.* **1982**, *76*, 4144.

(19) Carter, J. T.; Cook, D. B. *THEOCHEM* **1991**, *83*, 111, and references therein.

(20) Dang, T. T.; Motell, E. L.; Travers, M. J.; Clifford, E. P.; Ellison, G. B.; Depuy, C. H.; Bierbaum, V. M. *Int. J. Mass Spectrom. Ion Processes* **1993**, *123*, 171.

(21) Juranic, I. O.; Mihailovic, M. L.; Dabovic, M. M *J. Chem. Soc., Perkin Trans. 2*, **1994**, 877.

(22) Dorigo, A. E.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 2195. Dorigo, A. E.; Houk, K. N. *J. Org. Chem.* **1988**, *53*, 1650. Dorigo, A. E.; McCarrick, M. A.; Loncharich, R. J.; Houk, K. N. *J. Am. Chem. Soc.* **1990**, *112*, 7508.

(23) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, P. M. W.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. GAUSSIAN94, Revision C.4; Gaussian, Inc.: Pittsburgh, PA, 1995.

(24) Jungkamp, T. P. W.; Seinfeld, J. H. Submitted to *J. Chem. Phys.*

(25) Ochterski, J. W.; Petersson, G. A.; Montgomery, J. A. *J. Chem. Phys*. **1996**, *104*, 2598.

(26) Dean, A. M.; Bozzelli, J. W.; Ritter, E. R. *Combust. Sci. Technol.* **1991**, *80*, 63.

(27) Viskolcz, B.; Lendvay, G.; Körtvelyesi, T.; Seres, L. *J. Am. Chem. Soc.* **1996**, *118*, 3006.

(28) Gilbert, R. G.; Jordan, M. J. T.; Smith, S. C.; Pitt, I. G.; Greenhill, P. G. UNIMOL, version of October 27, 1992.

(29) Evleth, E. M.; Melius, C. F.; Rayez, M. T.; Rayez, J. C.; Forst, W. *J. Phys. Chem.* **1993**, *97*, 5040.

(30) Ing, J. Ph.D. Thesis, New Jersey Institute of Technology, 1996.

(31) Lias, S. G.; Liebman, J. F.; Levin, R. D.; Kafafi, S. A.; Stein, S. E. NIST Standard Reference Database 25 “Structure and Properties”, Vers. 2.01; National Institute of Standards and Technology: Gaithersburg, MD, 1994.