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A Quantum Chemical Study of the C−C Bond Fission Pathways of Alkoxy Radicals Formed following OH Addition to Isoprene

Theodore S. Dibble[†]

Department of Chemistry, College of Environmental Science and Forestry, State University of New York, 1 Forestry Drive, Syracuse, New York 13210

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Isoprene is one of the most important non-methane organic compounds in tropospheric chemistry, yet its atmospheric degradation pathways remain incompletely understood. The uncertain fates of alkoxy radicals formed in the first stages of the OH-initiated degradation of isoprene contribute significantly to our ignorance. This paper examines the C−C bond fission pathways of these radicals at the B3LYP/6-311G(2df,2p) level of theory. For the four β-hydroxyalkoxy radicals that are expected to be formed, C−C bond fission (decomposition) pathways exist with very low barriers (0.7−2.1 kcal/mol) that are likely to dominate the chemistry. These radicals appear to possess intramolecular hydrogen bonds which typically persist in the transition states. For the two δ-hydroxyalkoxy radicals formed, C−C bond fission is endothermic (16−20 kcal/mol) and this pathway is unlikely to be important.

I. Introduction

On a global basis, isoprene (2-methyl-1,3-butadiene) constitutes about 40% of the mass of non-methane organic compounds (NMOCs) emitted to the atmosphere.[1] Isoprene is emitted almost exclusively by natural sources, and is a significant means by which carbon is transferred from the biosphere to the atmosphere. Studies of plants indicate that isoprene is only emitted in sunlight and most copiously on hot windless days: ideal conditions for ozone production in the polluted troposphere.[2] Obviously, isoprene is one the most important NMOCs for ozone production in the lower atmosphere, and the pathways and products of its decomposition are a matter of considerable interest to atmospheric chemists concerned with air pollution.[3,4] In the daytime atmosphere, reaction with OH is the primary initiator of isoprene degradation.[5]

In the presence of NO_x, the primary products of the reaction of isoprene with OH are formaldehyde, methyl vinyl ketone ($CH_2{=}CH(O)CH_3$), methacrolein ($CH_2{=}C(CH_3)CH{=}O$), and 3-methylfuran, which together account for 65% of the products.[6−10] The balance of the products are expected to be a large number of organic nitrates and carbonyl compounds. However, only recently have atmospheric chemists acquired experimental verification of the rich variety of carbonyl products formed in isoprene degradation.[11] Despite this recent advance, yields of these products remain unknown and many have not been firmly identified. This incomplete data makes it difficult to determine the atmospheric reaction pathways of isoprene.

Efforts to elucidate the degradation pathways of isoprene are complicated by the presence of multiple sites of OH addition, the potential for transient intermediates to react via multiple pathways, and the high reactivity of the initial closed-shell reaction products. Analysis of the complex product mixture is rendered difficult by a general absence of authentic standards and the reactivity of many closed-shell products on the walls of gas chromatographs. However, the first three dominant steps in isoprene degradation are similar to those of other alkenes. Detailed descriptions have been given;[7−11] only a summary is presented here. Hydroxyl radical reacts almost exclusively by addition to the butadiene chain (reaction 1),[6] and the carbon-centered radicals thus formed add molecular oxygen to form a peroxy radical (reaction 2). Addition of OH to the terminal carbon atoms of the butadiene chain produces allylic radicals, which permits the subsequent addition of molecular oxygen to occur either β or δ to the OH group; addition to the internal carbon atoms permits only the β-addition of O_2. In this manner, six isomeric peroxy radicals are formed, which can then react with NO to form the six corresponding alkoxy radicals and alkylnitrates (reaction 3). The following illustrates the sequence:

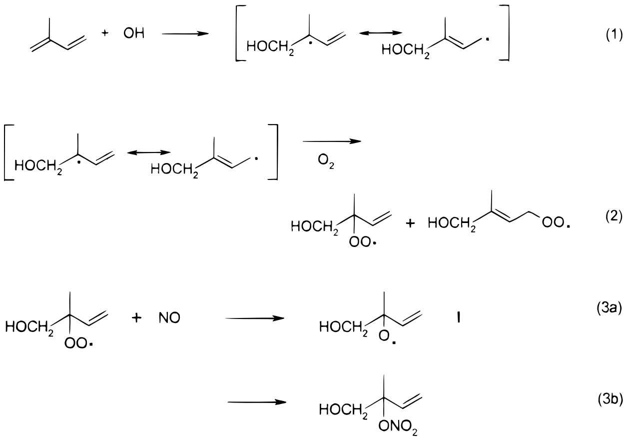

Figure 1 depicts the four β-hydroxyalkoxy radicals and two δ-hydroxyalkoxy radicals thus formed. In the numbering scheme adopted here, roman numerals **I**−**IV** correspond to the number of the carbon atom onto which OH has added in forming a β-hydroxyalkoxy radical; **V** and **VI** correspond to the δ-hydroxyalkoxy radicals formed by OH attack on carbons 1 and 4, respectively.

The fate of alkoxy radicals formed in reaction 3a is a significant point of uncertainty. Partial mechanisms have been

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[†] E-mail: tsdibble@mailbox.syr.edu.

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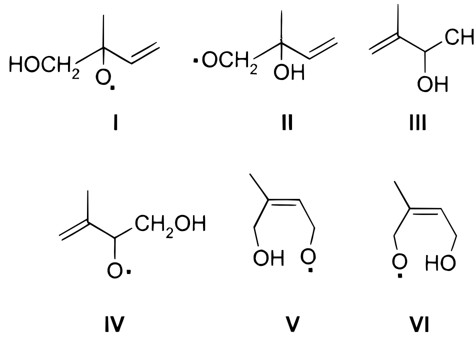
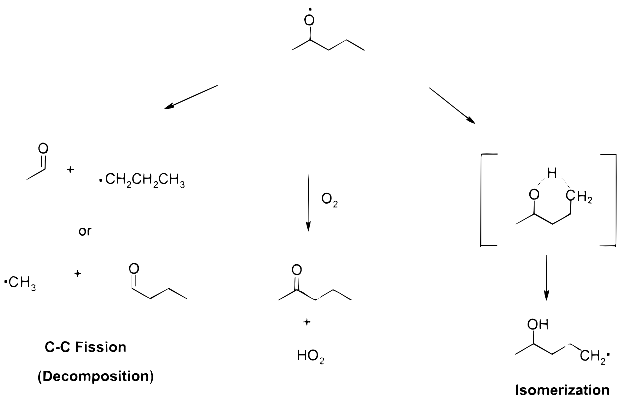


Figure 1. Structures of the six alkoxy radicals initially formed following OH addition to isoprene.

SCHEME 1



presented by Atkinson and co-workers[7,8] and Paulson and co-workers.[9,10] Both groups agree that **I** and **IV** react primarily by loss of $^{\bullet}CH_2OH$ to produce methyl vinyl ketone and methacrolein, respectively, and that radicals **II** and **III** react via loss of $CH_2{=}O$. The radical products of decomposition of **II** and **III** react with molecular oxygen to once again produce methyl vinyl ketone and methacrolein, respectively. Species **II** and **III** might also cyclize to form 3-methylfuran.[7,10,12] The fate of radicals **V** and **VI** is not established. Either isomerization or reaction with O_2 would produce hydroxycarbonyl compounds; isomerization might also lead to formation of 3-methylfuran.[7,9] Recently, Yu, Jeffries, and Le Lacheur[11] identified many previously unknown carbonyl products, and these authors invoked additional reaction pathways for these alkoxy radicals. For example, they found $C_4H_6O_2$ and suggested it was hydroxymethyl vinyl ketone formed from loss of CH_3 from **I**. They also found $C_5H_6O_2$, which they presumed to result from C−H fission at the α-carbon of **IV**. Jenkin has recently presented a revised mechanism for the initial steps of isoprene degradation.[12,13]

In general, alkoxy radicals in the atmosphere are expected to react with O_2, isomerize, or undergo C−C fission (decomposition), as illustrated in Scheme 1.[6,14] There have been few direct studies of the unimolecular reactions of alkoxy radicals, primarily due to a lack of direct probes of the C_4 and larger alkoxy radicals for which these reactions are relevant. Therefore, the present understanding of the unimolecular reactions of alkoxy radicals is derived primarily from product yield studies, and rates constants for the O_2 reaction with C_4 and larger alkoxy radicals are not well grounded in experiment.[14,15] In general, the rate of reaction with O_2 is thought to depend only a little on the structure of the alkoxy radical reactant, with $k_{298} \sim (6-10) \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}, implying a pseudo-first-order rate of $\sim 4 \times 10^4$ s^{-1} in 1 atm of air.[14−16] The presence of the β-hydroxy group appears to have no great effect on the rate.[17] By contrast, the rates of the isomerization and decomposition reactions depend enormously on structure. The isomerization reaction proceeds readily only if the transition state can form a six-member ring (the 1,5 H-shift shown in Scheme 1), in which case the rate constant is thought to be of the order of 10^6 s^{-1} under ambient conditions, and somewhat dependent on the substituents at the site of abstraction. The transition state for the five-member ring formed in the 1,4 H-shift is suggested to have about 6 kcal/mol of strain energy, rendering this reaction slow.[18,19] For the C−C fission reaction, a semiempirical rule developed by Choo and Benson[20] and modified by Atkinson[14] performs well in reproducing the relative rates of decomposition versus O_2 reaction for alkoxy radicals derived from alkanes (at 298 K in 1 atm of air). Atkinson suggests using a constant Arrhenius prefactor of 2×10^{14} s^{-1} and that the activation barrier may be computed from the enthalpy change for the decomposition reaction and the ionization potential of the leaving alkyl group.

In a few cases it has been observed[21−23] or proposed[11] that alkoxy radicals can undergo unimolecular C−H bond fission (in the absence of O_2) to form the corresponding carbonyl compound and a hydrogen atom. The hydrogen atom will subsequently react with O_2 to form HO_2, so the net effect is the same as reaction with O_2. The literature on this reaction is too sparse to build a model of the rate of this reaction, but it has primarily been observed with alkoxy radicals with ether linkages. Therefore, it might not be expected to be a competitive reaction of the radicals studied here.

Models of the rates of C−C fission and isomerization, based on data from alkoxy radicals derived from alkanes, do not perform nearly as well for β-hydroxyalkoxy radicals derived from alkenes.[14] No model exists for predicting the rate of C−H fission. Although progress is being made in obtaining laser-induced fluorescence spectra of specific isomers of “large” ($\geq C_4$) alkoxy radicals for use in direct kinetic studies,[24,25] it will be difficult to extend the experiments to the multifunctional alkoxy radicals considered here. Therefore, we have turned to quantum chemical methods to study this chemistry.

Species **I**−**VI** have seven heavy atoms and no symmetry, and are radicals. Clearly, one cannot directly apply high-level ab initio methods (such as CCSD(T) with triple-ζ basis sets) to the determination of the structures and energies of the transition states for their reactions. Less demanding ab initio methods might lack the desired accuracy, especially in light of the high spin contamination encountered.[26] However, density functional theory possesses the efficiency necessary for this task, and the better functionals are usually reliable for transition states.[27,28] Moreover, one of the better functionals (B3LYP, see below) has demonstrated good performance in previous studies of alkoxy radicals.[19,29−31] In this paper, the B3LYP functional is applied to determine the structures, vibrational frequencies, and energies of all six alkoxy radicals and the transition states and products for the atmospherically conceivable C−C bond fission pathways. Due to the large numbers of molecules and transition states considered, it was not reasonable to fully explore the conformational space of each species, but such exploration is carried out for one of the β-hydroxyalkoxy (**I**) and both δ-hydroxyalkoxy radicals. Also, to verify the accuracy of the activation barriers computed here, two of the reactions of species **I** are also studied using two of the complete basis set (CBS) methods: CBS-4 and CBS-q. Work is in progress to study reaction pathways for isomerization and C−H fission. The kinetics of the reaction with molecular oxygen is not likely to be a fruitful subject for quantum mechanical calculations, because the small activation barrier for this reaction depends on differences in energies between ROOO$^{\bullet}$ species that present some challenges to computation.[32−34] However, even without direct data on these alternative reaction pathways, the results of the present work enable one to draw fairly reliable conclusions about the likely fates of the β-hydroxyalkoxy radicals **I**−**IV**.

II. Computational Method

Computations were carried out using the GAUSSIAN94[35] and GAUSSIAN98[36] series of programs, except for some molecular mechanics computations that employed SPARTAN.[37] All radicals were treated with the unrestricted Hartree−Fock (UHF) formulation. Density functional theory (DFT) calculations used the HF exchange functional of Becke[38] and the correlation functional of Lee, Yang, and Parr,[39] a combination denoted B3LYP.

The radicals, transition states, and reaction products potentially access multiple conformations, the full exploration of which is outside the scope of this paper. The structure of the β-hydroxyalkoxy radicals **I**−**IV** was expected to include an intramolecular hydrogen bond from the hydroxyl group to the radical center, thus forming a five-member ring analogous to that found to be most stable in studies of $HOCH_2CH_2O^{\bullet}$.[30,31] In that molecule the gauche structure with an intramolecular hydrogen bond was found to be about 2−3 kcal/mol more stable than the next most stable (anti) structure. Because it is unclear whether this motif yields the lowest energy conformer for the larger β-hydroxyalkoxy radicals studied here, the conformational space of species **I** was explored at the B3LYP/3-21G level of theory starting from 27 initial conformations systematically generated in SPARTAN. For radicals **V** and **VI**, where 54 initial structures were generated, the conformational space was first explored using the Sybil molecular mechanics force field. The two most stable structures found by this method were subsequently optimized at B3LYP/3-21G and the one of lowest energy used in further calculations.

For studies of chemical reactions, all species were optimized at the B3LYP/6-31G(d) and B3LYP/6-311G(2df,2p) levels of theory. First guesses for transition state geometries were obtained, starting from the geometry of the corresponding radical, by increasing the length of the breaking C−C bond to ∼2.0 Å and performing a constrained optimization. The resulting geometry was then used for a direct transition state search. Reactant geometries also provided starting points for studies of some of the larger product species. The products were studied as isolated molecules rather than as the exit channel complexes that might be obtained in an intrinsic reaction coordinate calculation.[30,31] Harmonic vibrational frequencies were calculated at B3LYP/6-31G(d) to verify the nature of potential energy minima and transition states, and were used without scaling to calculate zero point energies (ZPE).

The goal of this work is to elucidate the degradation pathways of isoprene; therefore, it was deemed prudent to verify the precision of these calculations using a rather different theoretical approach. For this purpose we selected the complete basis set methods CBS-4 and CBS-q developed by Ochterski, Montgomery, Petersson, and co-workers,[40,41] and used them to determine the activation energy for the two most probable reactions of species **I**. The CBS-4 and CBS-q methods are the least expensive (computationally) in a series of methods designed to provide very accurate energies at relatively low computational cost. Both CBS-4 and CBS-q employ HF/3-21G geometries as the basis for a series of single-point calculations and empirical corrections. The single points include a large basis set Hartree−Fock calculation and a complete basis set extrapolation at the second-order Moller−Plesset level of theory. Higher level correlation is included at the MP4(SDQ) and QCISD(T) levels for the CBS-4 and CBS-q methods, respectively. While CBS calculations for potential energy minima are automated in GAUSSIAN94 and GAUSSIAN98, computations on transition states must be submitted and tabulated by the user. The accuracy of this tabulation was checked by submitting the CBS job for radical **I** both through the automated route and by hand. The individual components and final CBS energies were compared to verify the reliability of this work.

TABLE 1: Structures of the Alkoxy Radicals I−VI at the B3LYP/6-311G(2df,2p) Level of Theory (Distances in angstroms, Angles in degrees)[a]

parameter	**I**	**II**	**III**	**IV**	**V**	**VI**
C_1C_2	1.565	1.558	1.330	1.330	1.510	1.540
C_2C_3	1.513	1.504	1.506	1.514	1.340	1.348
C_3C_4	1.324	1.324	1.567	1.616	1.526	1.507
C_2C_5	1.567	1.538	1.502	1.500	1.505	1.506
$CO^{\bullet}$	1.362	1.358	1.352	1.338	1.380	1.376
CO	1.404	1.415	1.408	1.390	1.402	1.403
OH	0.965	0.966	0.967	0.964	0.971	0.981
$O^{\bullet}$--H	2.292	2.201	2.144	2.335	1.915	1.894
OH--$O^{\bullet}$	108.4	113.7	115.7	105.2	143.0	142.8
HOCC/OH--OC′ [b]	−49.0	−41.5	−36.5	−53.7	15.3	−16.1
$OCCO^{\bullet}$/C′C═CC[c]	51.8	−49.1	−46.4	57.9	−0.7	1.5

[a] Carbon atoms numbered by IUPAC convention (C_5 is the methyl carbon) [b] For radicals **I**−**IV**, the dihedral angle in this row is the covalently bonded chain HOCC, while for **V** and **VI** the entry refers to the dihedral angle OH−OC′ across the hydrogen bond. [c] For radicals **I**−**IV**, the dihedral angle in this row is $OCCO^{\bullet}$, while for **V** and **VI** the entry refers to C′C═CC.

III. Results and Discussion

The first issue to be addressed is the stability of the conformers. In our study of radical **I**, the structure with an intramolecular hydrogen bond did prove to be the most stable; the next lowest-lying structures were 0.9 and 2.3 kcal/mol higher in energy (ignoring ZPE). This result provides us some assurance that our initial geometries correspond to the minimum energy conformers for radicals **I**−**IV**. Both **V** and **VI** adopted structures with the $HOCH_2$− and $-CH_2O^{\bullet}$ groups cis to each other and forming an intramolecular hydrogen bond. It should be noted that uncertainty as to the identity of the lowest energy conformer is unlikely to have any significant influence on the activation barriers. For example, in Vereecken and Peters study of $HOCH_2$-$CH_2O^{\bullet}$, five conformers were obtained for the radical and three for the transition state.[31] For the three structures for which a one-to-one correspondence exists with the conformation of a transition state, the activation barriers were 9.6, 9.8, and 9.9 kcal/mol. A similar invariance of activation barriers was found for the decomposition of various conformers of $HOCH_2CH$-$(O^{\bullet})CH_3$.[42]

The structures of these radicals are of some interest. Table 1 lists selected geometric parameters of the radicals and Table 2 lists values for the transition states. The single bonds adjacent to double bonds all have lengths between 1.506 and 1.540 Å. Those C−C single bonds not adjacent to double bonds range in length from 1.538 to 1.567 Å, with one notable exception: the C_3−C_4 bond in **IV** is 1.62 Å long, much longer than the analogous C_1−C_2 bond in **I**. The C−$O^{\bullet}$ bond lengths are smaller than the C−OH bond lengths by 0.047−0.057 in species **I**−**IV**, while the difference is slightly larger in **V** and much smaller in **VI**. The hydrogen bonds formed in **I**−**IV** are long (2.1−2.3 Å)

TABLE 2: Structures of the Transition States for the C−C Fission Pathways of Radicals I−VI at the B3LYP/6-311G(2df,2p) Level of Theory (Distances in angstroms, Angles in degrees)

parameter	**[Ia]**	**[Ib]**	**[Ic]**	**[II]**	**[III]**	**[IVa]**	**[IVb]**	**[V]**	**[VI]**
C_1C_2	1.539	1.971	1.539	1.816	1.349	1.342	1.314	1.522	2.279
C_2C_3	1.494	1.501	2.172	1.476	1.466	1.495	2.245	1.306	1.305
C_3C_4	1.328	1.328	1.301	1.331	1.892	2.022	1.531	2.320	1.515
C_2C_5	2.091	1.531	1.522	1.520	1.507	1.504	1.473	1.519	1.471
$CO^\bullet$	1.251	1.270	1.238	1.286	1.277	1.266	1.238	1.224	1.228
CO	1.402	1.349	1.424	1.379	1.367	1.348	1.424	1.399	1.400
OH	0.970	0.968	0.963	0.967	0.981	0.982	0.972	0.971	0.972
$O^\bullet$--H	2.076	2.377	2.747	2.254	2.04	2.081	2.653	1.886	1.870
OH--$O^\bullet$	116.8	104.5	96.4	111.1	116.2	111.2	98.0	150.7	150.1
HOCC/OH--OC′ [a]	−27.6	−58.7	−62.4	−48.8	−41.8	−50.8	−58.9	−8.5	−12.2
$OCCO^\bullet$/C′C═CC[b]	28.5	57.3	79.8	−58.2	−50.8	51.0	76.5	−5.3	−2.9

[a] For transition states arising from radicals **I**−**IV**, the dihedral angle in this row is the covalently bonded chain HOCC, while for **V** and **VI** the entry refers to the dihedral angle OH−OC′ across the hydrogen bond. [b] For transition states arising from radicals **I**−**IV**, the dihedral angle in this row is OCCO, while for reactions of **V** and **VI** the entry refers to C′C═CC.

and possess rather sharp OH- -$O^\bullet$ angles (∼110°) due to the constraints imposed by forming five-member rings. In **V** and **VI** the hydrogen bonds are shorter (1.90 Å) and much less bent (143°).

In the transition states, lengths of the breaking C−C bonds range from 1.82 to 2.32 Å, but these lengths correlate directly with the activation barriers to reaction ($R^2 = 0.85$) and the energies of reaction ($R^2 = 0.95$). As an example, consider reactions II and V with breaking bond lengths of 1.82 and 2.32 Å in the transition states, activation energies of 0.7 and 19.5 kcal/mol, and energies of reaction of −12.8 and +20.3 kcal/mol, respectively. These results are in accord with Hammond's postulate that, in a homologous series of reactions, a more endothermic reaction has a more product-like transition state and thus a higher activation energy.[43,44] The intramolecular hydrogen bond of the radical appears to be retained in most of the transition states, even in those cases (**[Ib]** and **[IVa]**) where the $^\bullet CH_2OH$ groups participating in the hydrogen bonding are separating from the rest of the molecule. Because hydrogen bonding is present in both reactant and transition state, there is probably little effect on the activation barrier.[30,31,42] As compared to B3LYP/6-311G(2df,2p), calculated HF/3-21G transition state structures predict that that the breaking C−C bond is 0.09 Å longer in [**Ia**] and 0.17 Å longer in [**Ib**]. While these differences may seem impressive, they are unlikely to have large effects on the energies.

Table 3 lists B3LYP values for absolute energies and zero-point energies for all reactants, transition states, and products. Relative energies for the reactions are contained in Table 4, and Figure 3 depicts the potential energy profile for the three C−C fission reactions of **I**. Unless otherwise specified, relative energies cited in the text are at the B3LYP/6-311G(2df,2p) + Δ*ZPE* level of theory. Species **III** and **IV** are the most stable by just a few tenths of a kcal/mole over **II**. Species **I** is slightly (∼1 kcal/mol) less stable than its isomer **II**, yet chemical intuition and product yield studies suggest that **I** is the alkoxy radical most likely to be formed (the probability is controlled by the OH addition step). **V** and **VI** are least stable, being 3 kcal/mol higher in energy than **III** and **IV**. Relative energies vary little with basis set.

Before turning to the activation barriers, let us first consider the likely reliability of the computed activation barriers. The B3LYP hybrid functional is generally considered one of the most accurate of functionals, particularly for energies,[27,28] and the 6-311G(2df,2p) basis set is large enough to give reliable energies. The B3LYP functional has demonstrated good accuracy in previous studies of alkoxy radical reactions. For example, in test calculations on the favored decomposition pathway of 2-butoxy employing the 6-31G(d) and 6-311G(2df,2p) basis sets, calculated activation barriers were 12.9 and 11.0 kcal/mol, respectively,[45] only about 1 and 3 kcal/mol below of the 14.3 kcal/mol value suggested by Atkinson.[14] Jungkamp, Smith, and Seinfeld obtained an activation barrier of 11.8 kcal/mol for the same process at B3LYP/6-31G(d,p).[29] The B3LYP/6-31G(d,p) results of Dibble[30] and Vereecken and Peeters[31] for

TABLE 3: Absolute Energies (hartrees) and Zero-Point Energies (kcal/mol, at B3LYP/6-31G(d)) of Alkoxy Radicals, Transition States (in brackets), and Reaction Products

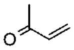
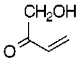
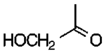
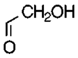
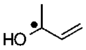
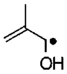
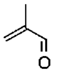
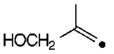
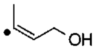
species	B3LYP/6-31G(d)	B3LYP/6-311G(2df,2p)	*ZPE*
I	−346.290 95	−346.416 64	83.6
II	−346.290 91	−346.417 10	83.0
III	−346.292 78	−346.418 07	83.4
IV	−346.292 41	−346.417 88	83.2
V	−346.291 37	−346.415 42	84.8
VI	−346.291 15	−346.415 24	84.7
[Ia]	−346.270 27	−346.398 60	81.5
[Ib]	−346.283 37	−346.411 39	82.4
[Ic]	−346.251 53	−346.381 08	80.8
[II]	−346.287 95	−346.414 91	82.3
[III]	−346.288 66	−346.415 22	82.4
[IVa]	−346.285 59	−346.413 13	82.3
[IVb]	−346.256 58	−346.385 29	81.0
[V]	−346.250 57	−346.379 31	81.6
[VI]	−346.257 61	−346.385 89	81.9
	−231.235 18	−231.316 23	56.4
	−306.442 90	−306.556 28	59.6
	−268.363 11	−268.464 55	56.1
$CH_3^\bullet$	−39.838 29	−39.856 37	18.7
CH_2O	−114.500 47	−114.543 20	16.8
$^\bullet CH_2OH$	−115.052 03	−115.102 97	23.5
$CH_2{=}CH^\bullet$	−77.901 21	−77.932 16	23.0
	−117.228 26	−117.271 38	41.3
	−229.035 78	−229.124 40	38.4
	−231.799 20	−231.888 39	62.5
	−231.793 71	−231.882 66	62.5
	−231.233 54	−231.314 33	56.5
	−231.743 51	−231.831 76	62.9
	−231.750 01	−231.837 93	62.5

TABLE 4: Activation Energies and Reaction Energies at 0 K (kcal/mol), Including ΔZPE

	activation energy		energy of reaction	
reaction	B3LYP/ 6-31G(d)	B3LYP/ 6-311G(2df,2p)	B3LYP/ 6-31G(d)	B3LYP/ 6-311G(2df,2p)
Ia	10.9	9.2	0.8	−2.8
Ib	3.6	2.1	−1.4	−5.3
Ic	21.9	19.5	12.2	8.0
II	1.2	0.7	−9.2	−12.8
III	1.6	0.8	−5.0	−9.0
IVa	3.4	2.1	1.1	−2.8
IVb	20.3	18.3	14.3	10.4
V	22.4	19.5	24.6	20.3
VI	18.2	15.6	20.1	16.0

$HOCH_2CH_2O^\bullet$ agree with experiment to within 1 kcal/mol.[17] Using these calculations as a guide, one expects the B3LYP/6-31G(d) results to underestimate the true activation barrier by about 1−2 kcal/mol. For the particular reactions studied here, the consistency of results across basis set and method provides additional reassurance as to reliability. Computed activation barriers for most of reactions studied here fall by 1−2 kcal/mol and the computed energies of reaction decrease by ∼4 kcal/mol when the basis set size is increased from 6-31G(d) to 6-311G(2df,2p). Also, spin contamination is low, with $\langle S^{**}2\rangle$ values typically 0.760 for the transition states and less for the radicals. The most direct test of the accuracy and reliability of the B3LYP results comes from the comparison with the CBS-4 and CBS-q results in Table 4. CBS-4 and CBS-q agree excellently with each other and with B3LYP. The exact agreement of the CBS-q and B3LYP/6-311G(2df,2p) activation barriers to reaction Ia is, of course, coincidental. The CBS methods, like B3LYP, have some tendency to underestimate activation barriers to alkoxy radical decomposition processes. For $HOCH_2CH_2O^\bullet$,[17] CBS-4 and CBS-q activation barriers were low by about 2 and 4 kcal/mol, respectively,[30] but for 2-butoxy these methods were lower than Atkinson's recommended value by about 7 and 6 kcal/mol, respectively.[45]

Finally, we turn to the chemistry. For radical **I**, the loss of $^\bullet CH_2OH$ in reaction Ib was found to have an activation barrier of only 2.1 kcal/mol and is therefore expected to dominate over loss of CH_3 (reaction Ia, $E_a = 9.2$ kcal/mol). Since the O_2 reaction is impossible and the 1,4 H-shift reaction (of a vynilic hydrogen!) slow, one can safely conclude that loss of $^\bullet CH_2OH$ is effectively the sole loss process for radical **I** under atmospheric conditions. Loss of vinyl radical (Ic) is, as expected, very slow, and this reaction possesses a significant barrier over and above its 8.0 kcal/mol endothermicity.

For both **II** and **III**, the only feasible C−C fission process produces formaldehyde and substituted allylic radicals. Computed activation barriers are below 1 kcal/mol in both cases, and exothermic by about 13 and 9 kcal/mol respectively. Both **II** and **III** have the potential to undergo isomerization, reaction with O_2, and C−H bond fission in addition to decomposition; there are also proposals that they could cyclize to yield 3-methylfuran.[7,10,12] Isomerization of **II** would require abstraction of a vinylic hydrogen, and will be slow, but **III** could isomerize by abstracting a hydrogen from the methyl group. However, the low activation barriers to decomposition combined with the suggested Arrhenius prefactor[14] of 2×10^{14} s^{-1} leads to 298 K rate constants of the order of 10^{13} s^{-1}, several orders of magnitude faster than the rates expected for isomerization (10^6 s^{-1}) or O_2 reaction (4×10^4 s^{-1}).[14] Therefore, unless unimolecular C−H fission or the cyclization reaction is fast enough to compete, one expects decomposition to be the sole fate of **II** and **III** under all atmospheric conditions.

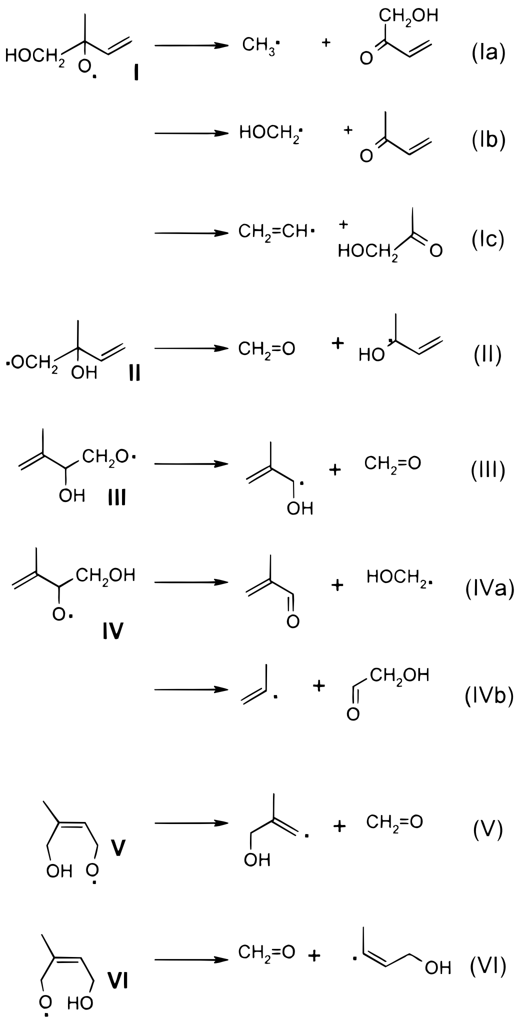


Figure 2. Carbon−carbon bond fission pathways for the six alkoxy radicals initially formed following OH addition to isoprene (reaction numbers in parentheses).

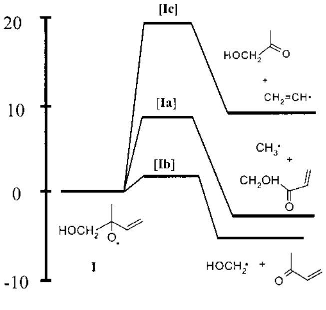


Figure 3. Potential energy profile for the C−C fission reactions of **I** at the B3LYP/6-311G(2df,2p) + ΔZPE level of theory (energies in kcal/mol).

Radical **IV** can feasibly undergo C−C fission either by loss of $^\bullet CH_2OH$ (IVa), or by loss of the $CH_3\dot{C}H{=}CH_2$ radical. The computations confirm chemical intuition about the relative instability of the latter radical: the 18 kcal/mol activation barrier renders this process atmospherically irrelevant. Loss of $^\bullet CH_2OH$ over a 2.1 kcal/mol barrier is expected to occur at a rate of about 10^{12} s^{-1}, about 6 orders of magnitude faster than the O_2 reaction (4×10^4 s^{-1}), which should be much faster than the 1,4 H-shift. Therefore, we expect that loss of $^\bullet CH_2OH$ via C−C fission will be the sole fate of **IV** in the atmosphere, unless C−H fission occurs at a competitive rate.

TABLE 5: Absolute Energies (hartrees) for I, [Ia], and [Ib] at the CBS-4 and CBS-q Levels of Theory, and Comparison of Activation Energies (kcal/mol) to Density Functional Theory

	absolute energies		relative energies			
species	CBS-4	CBS-q	CBS-4	CBS-q	B3LYP/6-31G(d)	B3LYP/6-311G(2df,2p)
I	−345.780 29	−345.833 81	0.0	0.0	0.0	0.0
[Ia]	−345.763 82	−345.819 21	10.3	9.2	10.9	9.2
[Ib]	−345.772 78	−345.829 90	4.7	2.5	3.6	2.1

The two δ-hydroxyalkoxy radicals are the only ones for which C−C bond fission appears relatively slow. In both **V** and **VI**, decomposition creates formaldehyde and a substituted vinyl radical, and the formation of vinylic radicals again possesses a significant activation barrier. In fact, the computed activation barriers are slightly lower than the computed energy of reaction. While basis set superposition error (BSSE) probably contributes to this, the existence of exit channel complexes along the pathway for C−C fission is also likely to be a major factor. The exit channel complex of $HOCH_2CH_2O^{\bullet}$ was found to be bound by about 5.5 kcal/mol;[30,31] this was reduced to 3.1 kcal/mol after correction for BSSE.[31] For **V** and **VI**, decomposition is predicted to occur at rates of about 1 and 700 s^{-1}, so both isomerization and reaction with O_2 will be much faster than decomposition. The potential also exists for C−H bond fission.

When assessing the likely accuracy of the calculations earlier in this section, it was suggested that the B3LYP/6-31G(d) energies might be low by 1−2 kcal/mol. However, propagating this error into the estimation of decomposition rates still suggests rate constants for C−C fission of **I**−**IV** that are 5 orders of magnitude faster than isomerization or O_2 reaction. Therefore, this uncertainty in calculated activation barriers does not change our conclusions regarding the fate of radicals **I**−**VI**. Our prediction that loss of $^{\bullet}CH_2OH$ from **I** and **IV** and CH_2O from **II** and **III** is faster than isomerization or O_2 reaction agrees well with the experimental findings of Atkinson and co-workers[7,8] and Paulson and co-workers.[9,10] However, the suggestion of Yu, Jeffries, and Le Lacheur that **I** can undergo loss of CH_3 (reaction Ia) appears incorrect, and the exceedingly high predicted rate for C−C fission of **IV** (10^{12} s^{-1}) casts doubt on their suggestion that C−H fission is competitive.[11] Furthermore, the low activation barrier to dissociation of **II** and **III** suggests that the proposed cyclization reaction would have to be exceedingly fast to be competitive; this undermines suggestions[7,10,12] that these radicals are the sources of 3-methylfuran. Product yield studies indicate that ∼25% of the primary yield from OH initiated oxidation of isoprene is an assortment of unquantified carbonyl and hydroxycarbonyl species. If one assumes that C−H bond fission is so slow as to be unimportant to the fate of alkoxy radicals **I**−**IV**, then our results imply that this 25% of the products are derived exclusively from radicals **V** and **VI**.

Let us consider the potential for direct experimental studies of these radicals. First, alkoxy radicals **I**−**IV** possess such low activation barriers to dissociation that their thermal lifetimes at 298 K and 1 atm are only picoseconds. Even if the present work significantly underestimates the stability of **I**−**IV**, these radicals will be very difficult to probe in the laboratory. This becomes clear when one considers techniques for producing these radicals. In the polluted troposphere these radicals will be formed by $RO_2 + NO$ reactions such as (3a). These reactions are exothermic, and it has been shown that significant fractions of some alkoxy radicals formed via $RO_2 + NO$ reactions possess sufficient internal energy that they promptly dissociate and are not completely quenched even at 1 atm pressure.[17,46] Activation barriers in these cases were about 10 kcal/mol, much larger than the ∼1−2 kcal/mol barriers computed for the dissociation of **I**−**IV**. Photolytic sources of alkoxy radicals could hardly avoid depositing a few kcal/mol of internal energy in the radicals, causing them to dissociate promptly. Thermoneutral $RO_2 + RO_2$ reactions are general sources of alkoxy radicals, but these reactions may be too slow to generate detectable concentrations of species as labile as **I**−**IV**. Therefore, it seems unlikely that kineticists will be able to directly study these radicals in the gas phase, and verification of the conclusions drawn here about radicals **I**−**IV** will rely on studies of their reaction products. By constrast, **V** and **VI** are quite stable with respect to dissociation, and might well be stable on a microsecond time scale with respect to other unimolecular reactions at subambient temperatures. Moreover, the instability of **I**−**IV** suggests that spectroscopic probes for **V** or **VI** would not face interferences from **I**−**IV**. Therefore, it might be possible to conduct laboratory studies of radicals **V** or **VI**.

Hydroxyalkoxy radicals of the type studied here present opportunities for fascinating basic research. In addition to the marvelous variety of competing chemical reactions that they may undergo, one might expect to find compelling spectroscopic and dynamical phenomena as a result of the intramolecular hydrogen bonds to radical centers which appear to be general features of hydroxyalkoxy radicals. Tunneling of the hydrogen atom between the two oxygens of a hydroxyalkoxy radical should lead to some interesting spectroscopy, yet there have been no theoretical or experimental studies of this phenomenon. The fact that these hydrogen bonds appear to persist in the transition states for C−C fission reactions that ultimately break that hydrogen bond implies the existence of exit channel complexes composed of a radical donating a hydrogen bond to a carbonyl compound, as was found for $HOCH_2CH_2O^{\bullet}$ [30,31] and $CH_2CH(O^{\bullet})CH_3$.[42] The persistence of the hydrogen bond in the transition state should have interesting consequences for the dynamics of these reactions.

IV. Conclusions

Density functional theory calculations with a reliable functional and a large basis set have been used to provide insight into the fate of the alkoxy radicals formed following OH addition to isoprene. CBS-4 and CBS-q calculations for two of the nine reactions confirm the reliability of this approach. For the β-hydroxyalkoxy radicals **I**−**IV**, C−C bond fission has an extremely low barrier and is expected to be the dominant process unless C−H bond fission of **II**−**IV** or cyclization of **II** or **III** is extremely fast. For the δ-hydroxyalkoxy radicals **V** and **VI** decomposition is slow and some other process will control their fates. The rapidity of decomposition of **I**−**IV** implies that it will be difficult to study these radicals directly in the laboratory, but **V** and **VI** are more amenable to detection and monitoring.

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