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Isomerization of OH-Isoprene Adducts and Hydroxyalkoxy Isoprene Radicals

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This paper employs quantum chemical methods to investigate gaps in our understanding of the fates of radical intermediates in the OH-initiated degradation of isoprene. We employ two density functional theory (DFT) approaches: the well-known B3LYP functional and the recently constructed MPW1K functional. The Complete Basis Set method CBS-QB3 is used selectively to verify certain DFT results. The paper focuses on the configuration of the isoprene-OH adducts with the hydroxyl radical bound to carbons 1 or 4 of isoprene and the fate of the δ-hydroxyalkoxy radicals produced from these adducts. The chemically activated isoprene-OH adducts undergo prompt E/Z isomerization in competition with quenching. This reaction allows formation of the δ-hydroxyalkoxy radicals possessing the (Z) configuration, enabling a fast 1,5 H-shift reaction to dominate the fate of these radicals. The (E) isomer of the δ-hydroxyalkoxy radical that cannot undergo a 1,5 H-shift is predicted to react exclusively with O_2. The (E) isomer of the δ-hydroxyalkoxy radical appears likely to undergo a 1,5 H-shift reaction, but that conclusion depends more sensitively than the other conclusions on the assumed rate of the O_2 reaction. The effect of tunneling, which has been ignored in most previous calculations of the rate constants of 1,5 H-shift reactions, is estimated using an asymmetric Eckart potential.

Introduction

Isoprene (2-methyl-1,3-butadiene) emissions to the atmosphere by vegetation constitute about 40% of the total mass of nonmethane organic compounds emitted to the atmosphere.[1] Isoprene is the dominant source of summertime ozone in North America,[2] and is a major source of HOOH to the lower atmosphere.[3] The obvious importance of isoprene has inspired numerous investigations of its atmospheric degradation. Chamber experiments have succeeded in quantifying about 75% of the products of isoprene degradation in polluted air.[4−8] More recent studies have used structure−activity relationships,[9] quantum computations,[10−15] and real time monitoring of radical intermediates[11,13,16,17] to investigate isoprene chemistry and kinetics.

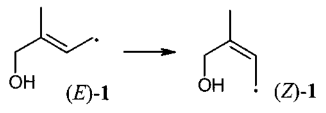
The first three steps in isoprene degradation are believed to be similar to those of other alkenes,[18] and are depicted in Figure 1. Hydroxyl radical attack is dominated by addition to carbons 1 and 4 of the butadiene chain. Subsequent reactions lead to production of four β-hydroxyalkoxy radicals and two δ-hydroxyalkoxy radicals. The β-hydroxyalkoxy radicals undergo C−C bond scission reactions leading to methacrolein and methylvinyl ketone, with formaldehyde and HO_2 as coproducts.[4,6,10,14] The fate of the δ-hydroxyalkoxy radicals is believed[19,20] to involve 1,5 H-shift reactions, exemplified below for 1-butoxy radical

$$CH_3CH_2CH_2CH_2O\cdot \rightarrow \cdot CH_2CH_2CH_2CH_2OH \qquad (1)$$

and/or reaction with O_2 to produce HO_2 and the corresponding carbonyl compound.

As noted by Paulson and Seinfeld,[19] the feasibility of the 1,5 H-shift reactions of the δ-hydroxyalkoxy radicals (**V** and **VI**) should depend on whether the alkoxy radicals are in (E) or (Z) configurations, because their configuration constrains the ability of **VI** to form the six-member ring transition state and changes the nature of the abstracted H-atom in **V**. Unfortunately, the extent of formation of (E) versus (Z) isomers of these alkoxy radicals is not known. Previous computational studies of these radicals considered only the (Z) isomers, which are expected to be lower in energy than the (E) isomers as a result of their intramolecular hydrogen bonds. However, about 95% of isoprene exists in the trans form.[21−23] Hydroxyl radical addition to one of the terminal carbons of *trans*-isoprene with retention of configuration leads to the (E) isomer of **1** and the (Z) isomer of **4**. As shown in Figure 1, retention of configuration in the subsequent chemistry would produce exclusively the (E) isomers of the corresponding δ-hydroxyalkoxy radicals **V** and **VI**.

Will the configuration be retained? Rotation about the double bond of the peroxy radical analogues of **V** and **VI** is expected to have so large a barrier as to be unimportant under ambient conditions. By contrast, the rotations about the allylic centers in adducts **1** and **4**



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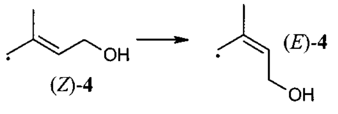

(3)

will possess much lower barriers to E−Z isomerization. However, by analogy to allyl radical,[24,25] it is likely that these barriers are nonnegligible, in contrast to the implicit assumption of Paulson and Seinfeld,[19] who proposed a 50:50 mixture of (E) and (Z) isomers. The (Z) isomers of the δ-hydroxyalkoxy radicals produced after reactions 2 and 3 will be more likely to

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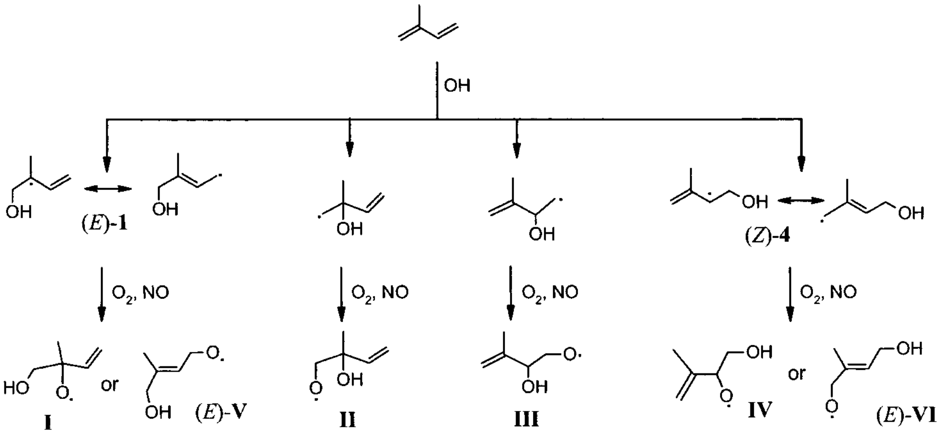

Figure 1. Initial pathways in the OH-radical initiated degradation of isoprene, assuming retention of configuration of isoprene-OH adducts **1** and **4**. The conversion of alkyl radical R to alkoxy radical RO, depicted as one step in the Figure, is the result of the consecutive reactions: $R + O_2 \rightarrow RO_2$ followed by $RO_2 + NO \rightarrow RO + NO_2$.

undergo the H-shift reaction than the (E) isomers, leading to different products and different effects on ozone production. Therefore, we need to investigate the feasibility of the thermal and chemically activated isomerization of the isoprene-OH adducts in order to understand the subsequent chemistry.

The reaction of an alkoxy radical with O_2 is commonly assumed to occur with $k_{298} = 6-10 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}, corresponding to pseudo-first-order rate constant of $\sim 4 \times 10^4$ s^{-1} in 1 atm of air.[26-28] It should be noted that recent work in our laboratory calls into question the generality of this rate constant.[29,30] Computational studies of these reactions would appear to require very time-consuming calculations, and are not pursued here.[31,32] Our present understanding of 1,5 H-shift reactions is derived primarily from relative rate studies;[26,27,33] real-time monitoring of products of subsequent chemistry;[28] and, more recently, computations.[32-36] A weakness in this database is the complete absence of kinetic studies in which the time rate of change of concentration of alkoxy radical has been monitored directly. The 1,5 H-shift reaction is thought to occur with a rate constant of about 3×10^5 s^{-1} under ambient conditions; the 1,4 and 1,6 H-shifts are much slower.[34,37] Mass spectral analysis of the contents of smog chambers provides some support for the formation of the products predicted by Paulson and Seinfeld[19] to form after isomerization of **V** and **VI**.[7,38]

The computational methods are described below. We then consider the activation barriers to the E/Z isomerization of the isoprene-OH adducts and an RRKM-Master Equation analysis of the extent of the prompt E/Z isomerization of chemically activated adducts. Then the potential for the (E) and (Z) isomers of **V** and **VI** to undergo H-shift reactions are considered. Finally, consequences for our understanding of ozone production from isoprene are discussed.

Computational Method

Computations were carried out using the GAUSSIAN98 series of programs;[39] the molecular mechanics module of Spartan[40] was used to obtain initial geometries of the isoprene-OH adducts. All radicals were treated with the spin-unrestricted formalism. Density functional theory (DFT) calculations used the Hartree–Fock exchange functional of Becke[41] and the correlation functional of Lee, Yang, and Parr,[42] a combination denoted B3LYP. The energies of some reactants and transition states were reevaluated using the MPW1K functional of Lynch and co-workers.[43] This functional is a modification of the functional known as MPW1PW91.[44]

The species we are studying can exist in many different conformations, and it is desirable to find the lowest energy conformation. The (Z) isomers of the alkoxy radicals **V** and **VI** were studied by us in a previous paper,[10] and information about the selection of their conformers may be found there. Note that the geometric parameters of the wrong conformer of (*E*)-**V** was reported in ref 10. For the isoprene-OH adducts and the (E) isomers of **V** and **VI**, we took the lowest 5–6 structures generated from Spartan's molecular mechanics module and determined the lowest energy conformer at the B3LYP/6-31G(d,p) + zero point energy (ZPE) level of theory. Structures of isoprene-OH adducts and the transition states for their E/Z isomerization were optimized at the B3LYP/6-31G(d,p) level of theory and refined at B3LYP/6-311G(2df,2p). For alkoxy radicals **V** and **VI** and their transition states, as in our previous work, we use B3LYP/6-31G(d) as the smaller basis set rather than 6-31G(d,p) and again use B3LYP/6-311G(2df,2p) to refine the calculations. Harmonic vibrational frequencies were calculated at B3LYP with either the 6-31G(d) or 6-31G(d,p) basis set to verify the nature of potential energy minima and transition states and were used without scaling to calculate zero point energies (ZPE). The values of selected reaction energies and activation barriers were refined using the Complete Basis Set (CBS) approach known as CBS-QB3,[45] which determines the energy of a species from a series of energy calculations and corrections terms at the B3LYP geometry.

Transition states for the E/Z isomerization were found by rotating the dihedral angle to ~90° and directly searching for the transition state. For the 1,5 H-shift reactions we first optimized the geometry while constraining the length of both the breaking C–H bond and the forming O–H bond to ~1.25 Å; this constraint was released for a direct transition state search. All transition states possess only a single imaginary frequency. We carried out intrinsic reaction coordinate calculations to verify the nature of the transition states for the *E*/*Z* isomerization. To verify the nature of the transition states for the 1,5 H-shift we confirmed that the motion of the imaginary vibrational frequency was characteristic of the expected reaction.

The validity of the B3LYP method for the *E*/*Z* isomerization of the allylic isoprene-OH adducts is supported by the success of the same approach (in fact, most computational methods) for the similar reaction in allyl radical, itself.[24,25] The activation energy and energy of reaction were recalculated at CBS-QB3, and these values are used in the RRKM–Master Equation calculations. For the 1,5 H-shift reaction of 1-butoxy radical ($CH_3CH_2CH_2CH_2O\cdot$), the error in the B3LYP approach appears

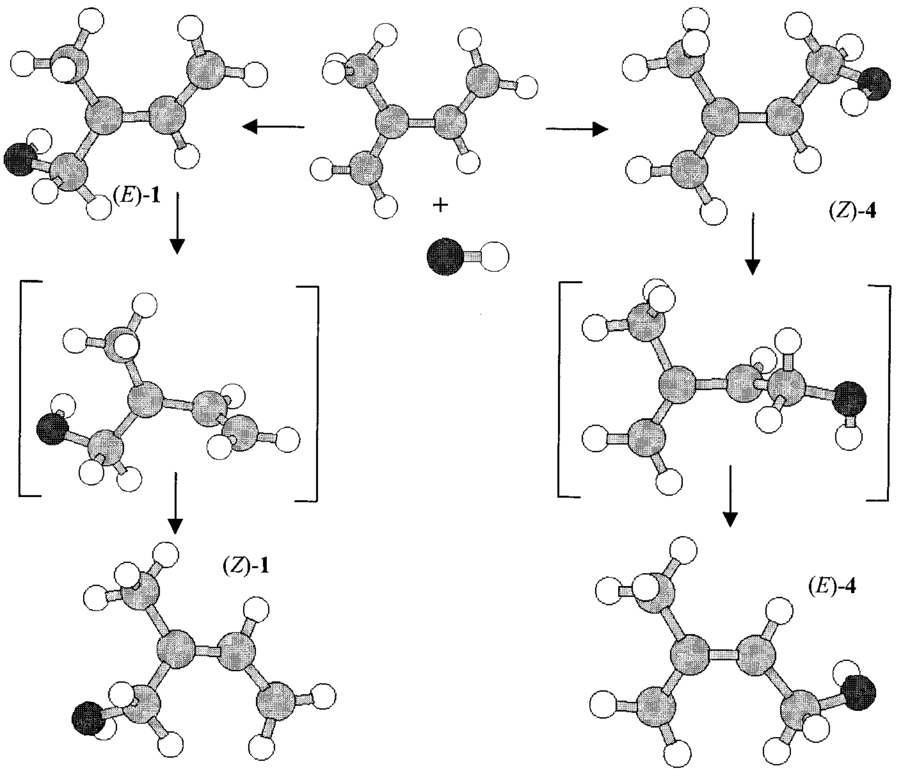

Figure 2. Structures of *trans*-isoprene, OH radical, (E) and (Z) isomers of isoprene-OH adducts **1** and **4**, and the transition states for the E−Z isomerization reactions (in brackets).

to be less than 1 kcal/mol using 6-31G(d,p).[32,34,35,46] However, B3LYP has a general tendency to underestimate activation barriers to H-atom transfer reactions.[43,47,48] Therefore, geometries of reactants and transition states for the 1,5 H-shift reactions were recalculated using the recently developed MPW1K functional of Lynch.[43] The MPW1K functional does an excellent job of determining activation barriers for a range of H-atom transfer reactions of small molecules.[43,48] MPW1K geometries were determined using both the 6-31G(d,p) and 6-311G(2df,2p) basis sets, and harmonic vibrational frequencies were calculated at 6-31G(d,p). The activation barrier for the 1,5 H-shift reaction of 1-butoxy radical was determined at MPW1K as one small check of the performance of this functional for this class of alkoxy radical reactions.

The potential for the prompt E/Z isomerization of chemically activated isoprene-OH adducts was examined using the MultiWell program of Barker.[49,50] The binding energy of adducts **1** and **4** was taken to be 34.8 and 32.3 kcal/mol, respectively, from the study of Lei et al.[12] (see also ref 13). Energy transfer parameters were chosen following the guidelines of Barker, Yoder, and King[51] to be $\alpha(E) = 40\ \text{cm}^{-1} + 0.025(E')$, where the probability of transfer of population from energy E' to a lower energy E is proportional to $\exp\{-(E' - E)/\alpha(E)\}$. Lennard-Jones parameters were chosen following the method suggested by Gilbert and Smith[52] and implemented for the same species by McGivern et al.[11] as $\sigma = 6.0$ Å and $\epsilon = 476$ K. The number of Monte Carlo trials was set at 10 000 to provide a statistical uncertainty of 0.005 for the fraction of each isomer. Unscaled harmonic vibrational frequencies were used to determine the densities of states.

To calculate rate constants for the 1,5 H-shift reactions, we use the UNIMOL program of Gilbert and Smith.[52,53] MPW1K frequencies, rotational constants, and (except where specified) activation barriers were used in all UNIMOL calculations. Lennard-Jones parameters were $\sigma = 6.4$ Å and $\epsilon = 476$ K.

Results and Discussion

Unless otherwise specified, B3LYP and MPW1K relative energies cited in the text are derived from 6-311G(2df,2p) optimized geometries and include differences in zero point energy calculated using either the 6-31G(d) or 6-31G(d,p) basis set, as specified above. See the Supporting Information for a listing of absolute energies and zero point energies, and Cartesian coordinates of all species.

E−Z Isomerization of the Isoprene-OH Adducts. Figure 2 depicts the structures of the (E) and (Z) isomers of isoprene-OH adducts **1** and **4**, and the transition states for the E/Z isomerization reactions. Other authors have discussed the structure of the isoprene-OH adducts, and our results are similar to theirs.[12,13] In the transition state to isomerization, the dihedral angle of the carbons of the isoprene backbone, ϕ(C1−C2−C3−C4), is −84.8° for adduct **1** and −100.6 degrees for adduct **4**. The potential energy profile for the E/Z isomerizations of **1** and **4** are depicted in Figure 3. Using CBS-QB3 (B3LYP), the (E) isomer of adduct **1** is more stable than the (Z) isomer by 0.8 (0.9) kcal/mole and the activation barrier for the (E) → (Z) reaction is 15.1 (15.5) kcal/mole. For adduct **4**, a barrier of 15.5 (13.8) kcal/mole separates the (Z) and (E) forms, and the (Z) isomer is 0.6 (0.1) kcal/mole more stable than the (E) isomer. Results for CBS-QB3 are mostly very close to the B3LYP results, and results are nearly independent of which of the two basis sets is employed at B3LYP; this supports the reliability of these results. These activation barriers are very similar to that determined for allyl radical, itself (15.7 ± 1 kcal/mol).[24] Given the Arrhenius preexponential factor of about $10^{13.5}$ s^{-1} from our MultiWell calculations (in the high-pressure limit) and experiment, rate constants slower than 10^{3} s^{-1} are implied at 298 K and 1 atm.

Given the slow rate constant calculated above, the thermal *E*/*Z* isomerization is not likely to compete with the addition of

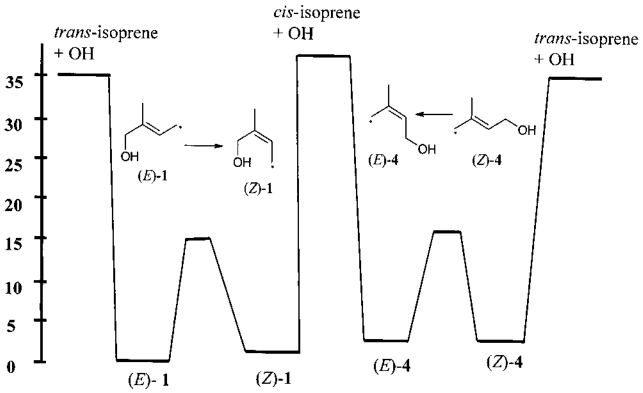

Figure 3. Potential energy profile for the formation and E/Z isomerization reactions of adducts **1** and **4** (energies in kcal/mole). The well depth with respect to *trans*-isoprene is from ref 12 at the CCSD(T)/6-311G(d,p) level of theory, and the barrier heights are at the CBS−QB3 level of theory. The energy difference between cis- and trans-isoprene is derived from experiment (refs 21 and 22).

O_2, a process with a pseudo-first-order rate constant of greater than 10^6 s^{-1} in 1 atm of air at 298 K.[17] However, the Multiwell[49,50] calculations indicate that the prompt isomerization of the chemically activated adducts does compete with quenching of the excess energy of the reaction. Using the parameters specified in the Methods section, we find for adduct **1** that the (*E*):(*Z*) branching ratio is 0.56:0.44 in 760 Torr N_2 at 298 K. This value is unchanged upon variation of the binding energy by 2.5 kcal/mol or by a factor of ~2 change in the average energy transferred in deactivating collisions. It does not depend on whether we assume the adducts start in a (shifted) thermal or monotonic distribution of energy. The yield of the (Z) isomer fell to 0.40 and 0.39 upon a 2.5 kcal/mol increase and decrease, respectively, in the activation energy. The relative energy of the two adducts was, of course, very significant: an error of 0.8 kcal/mol (100%) in the relative energies changes the branching ratios by 0.13. Of interest to experimentalists working at subambient pressure, the (Z)/(E) branching ratio was barely affected by pressure, being 0.58:0.42, 0.60:0.40, and 0.62:0.38 at 100, 10, and 1 Torr, respectively.

In contrast, the branching ratio for the (Z) → (E) isomerization of **4**, initially calculated as 0.42, was a strong function of simulation parameters. For example, upon a 2.5 kcal/mol decrease or increase in the model value of the activation barrier, the yield of the (E) isomer increased to 0.65 and decreased to 0.11, respectively. The very different sensitivities of the calculations for **1** and **4** are readily explained. For both adducts, a significant fraction of the initially formed configuration promptly (<0.1 ns) isomerizes to the other configuration. As the average internal energy of the excited molecules decrease, the system continually seeks to reestablish a new E/Z ratio. This continues until the system reaches an energy, call it the quitting energy, where isomerization becomes much slower than further deactivation; the ratio at this point determines the final E/Z ratio. Obviously, the quitting energy is quite sensitive to the activation energy. In the case of adduct **1**, the ratio of the density of states of the two isomers changes little with energy, so the E/Z ratio is nearly independent of the simulation parameters. For adduct **4**, the ratio of the density of states depends strongly on energy, and hence, the final ratio depends strongly on the value of the quitting energy (activation energy). Furthermore, the ratio of the density of states in **4** changes more rapidly with energy that the E/Z ratio can change; therefore, the simulation results are also sensitive to the initial energy of the radicals and the energy transfer parameters. The difference in the computed ratio of the density of states of the two pairs of E/Z isomers may arise from the computed (harmonic) vibrational frequencies used in the calculation: there is a close match between the vibrational frequencies of the (E) and (Z) isomers in **1** but not in **4**. Specifically, the (E) isomer of **4** has a very low-frequency mode (50 cm^{-1}) for which there is not a corresponding very low-frequency mode in the (Z) isomer.

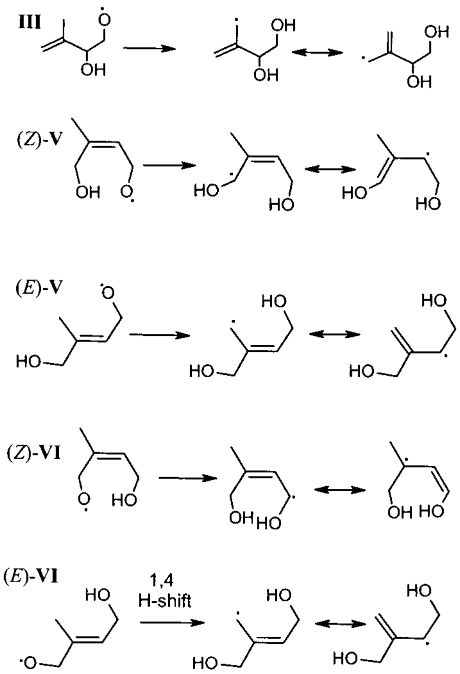

Figure 4. H-shift reactions of hydroxyalkoxy radicals from isoprene. All these reactions are 1,5 H-shift reactions, except for that of (*E*)-**VI**, which is labeled 1,4 H-shift.

A more proper treatment of low-frequency vibrational modes (as internal rotations) might lead to more robust results for the E/Z ratio of adduct **4**. However, examination of the vibrational modes of the two isomers of adduct **4** and the transition state for E/Z conversion did not suggest a consistent and unambiguous way to carry this out. Despite these uncertainties, the results clearly indicate that both the E and Z isomers of the adducts **1** and **4**, and hence, both the (E) and the (Z) isomers of alkoxy radicals **V** and **VI** will be formed to a significant extent.

1,*n* H−Shift Reactions the Alkoxy Radicals. Figure 4 depicts the five H-shift reactions considered. We briefly consider radical **III**, the only β-hydroxyalkoxy radical for which a 1,5 H-shift is feasible (from the methyl group). The conformer of radical **III** that can undergo the H-shift reaction must have the radical center oriented properly with respect to the methyl group (as depicted in Figure 4). This conformer is 4.0 kcal/mol higher in energy (at B3LYP/6-31G(d)) than the more stable conformer described in ref 10. In the transition state, the breaking C−H bond and forming O−H bonds are 1.28 and 1.30 Å long at B3LYP/6-311G(2df,2p) (1.26 and 1.28 Å at MPW1K); because a normal C−H bond is ~0.1 Å longer than a normal O−H bond, this indicates a transition state that is closer to reactants than products. The intramolecular hydrogen bond to the alkoxy radical center appears to be intact in the transition state, and is nearly the same length (2.22 Å) as in the stable conformer of radical **III**, itself (2.25 Å).

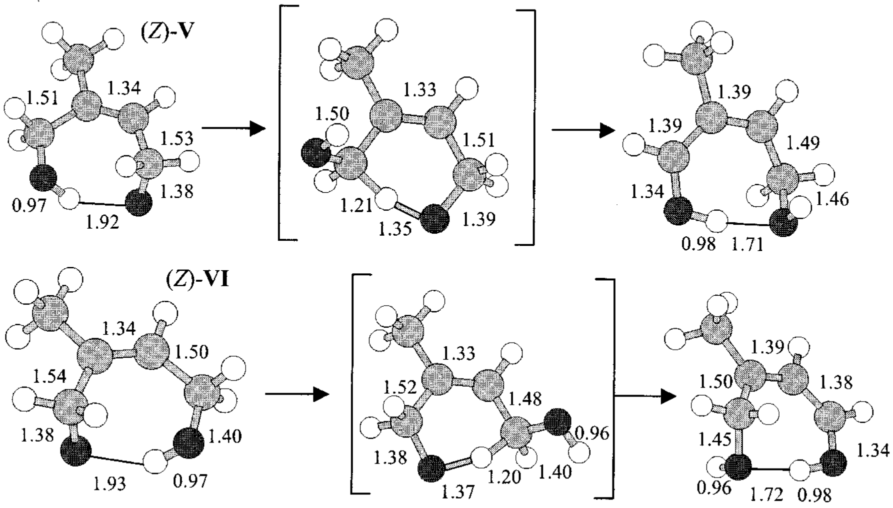

Figure 5. Structures of the (E) and (Z) isomers of alkoxy radicals **V** and **VI**, the transition states for their 1,5 H-shift reactions (in brackets), and the products of the 1,5 H-shift reactions. Thin lines represent hydrogen bonds. Numbers are lengths, in Å of C−C, C−O, O−H bonds, and OH−O hydrogen bonds, at the B3LYP/6-311G(2df,2p) level of theory. In the transition states the lengths of breaking C−H bonds and forming O−H bonds are also specified.

The transition state for isomerization is calculated to be 8.5 kcal/mol (B3LYP) or 11.5 kcal/mol (MPW1K) above the *more stable* conformer, and that is the value most relevant to estimating the rate constant. Using the MPW1K (B3LYP) barriers, we obtain a rate constant of 3×10^3 s^{-1} (5×10^5 s^{-1}) at 298 K and 1 atm air. The decomposition reaction possesses a barrier of only 1.6 kcal/mol at B3LYP, but even the 5.6 kcal/mol decomposition barrier computed by Lei and Zhang[14] at CCSD(T) suggest a rate constant ($k_{dec} = 6 \times 10^8$ s^{-1}) a thousand to a million times faster than that for the 1,5 H-shift. These results indicate that decomposition is much faster than the 1,5 H-shift reaction or the expected rate for reaction with O_2 in 1 atm of air at 298 K.

Figure 5 depicts the structures of the (Z) isomers of **V** and **VI**, the transition states for their 1,5 H-shifts, and the products of those reactions. For the transition state in (*Z*)-**V**, the breaking C−H and forming O−H bond lengths are 1.21 Å (1.20 Å) and 1.35 Å (1.33 Å) at the B3LYP (MPW1K) level of theory with a 6-311G(2df,2p) basis set. For (*Z*)-**V**, itself, the length of the OH−O hydrogen bond is 1.92 Å (1.95 Å). As can be seen from Figure 5, the structural parameters for (*Z*)-**VI** and its transition state are very similar to those for (*Z*)-**V**. Both transition states are structurally more similar to reactants than products, in accord with the predictions of Hammond's postulate[54] for these highly exothermic reactions. The agreement between these two functionals is reassuring. For (*Z*)-**VI** and the transition state to its 1,5 H-shift, the differences in bond lengths between the two functionals are of the same sign and similar magnitude. The products of these 1,5 H-shift reactions are allylic, as shown in Figure 4. Figure 5 depicts the (Z) isomers of these radicals, each of which has the potential for hydrogen bonding. The more stable hydrogen bond motif would appear to be the one with the −OH group on the allylic radical center donating to the oxygen of the newly formed −OH group, as shown.

The calculated barriers to the 1,5 H-shift reactions of the (Z) isomers of **V** and **VI** (from $-CH_2OH$ groups) are only 2.1 and 2.4 kcal/mol, respectively, at B3LYP, but are 5.4 and 5.2 kcal/mol using MPW1K. We use the UNIMOL program to determine a rate constant at 298 K and 1 atm of air; we conservatively and, probably, realistically, (see the Methods section) take the higher activation barriers yielded by the MPW1K functional, This calculation obtains rate constants of 8.5×10^7 s^{-1} and 1.0×10^8 s^{-1} for (*Z*)-**V** and (*Z*)-**VI**, respectively. These results are over 3 orders of magnitude faster than the expected rate of reaction with O_2, and about six orders (eight) of magnitude faster than the rates of decomposition computed by Lei and Zhang[14] (estimated by us,[10] previously). The reported uncertainty of 2 kcal/mol in the MPW1K activation energy[48] (a factor of about 30 in rate constant at 298 K) does little to alter the conclusion that the atmospheric fate of these radicals will be almost entirely the 1,5 H-shift reaction.

The 1,5 H-shift reactions of the (Z) isomers of **V** and **VI** are exothermic by about ∼28 kcal/mol; this is in strong contrast to the nearly thermoneutral 1,5 H-shift of 1-butoxy and the ∼14 kcal/mol exothermicity of the 1,5 H-shifts of **III** and (*E*) **V** and the 1,4 H-shift of (*E*) **VI** (see Table 1 for data). This might largely be explained by the intramolecular hydrogen bonds present in the (Z) isomers of **V** and **VI**, and the greater stability of resonance structures of the (Z) isomers of **V** and **VI** versus the (E) isomers or radical **III** (See Figure 4).

The activation barrier to the 1,5 H-shift of (E) isomer of **V** (from the $-CH_3$ group) is 8.4 kcal/mol at B3LYP and 11.6 kcal/mol at MPW1K. We note that the presence of an −OH group at the site of abstraction of the (Z) isomer is the apparent source of the large difference in the computed barriers to the 1,5 H-shift reactions of the (Z) and (E) isomers of **V**. At both B3LYP and MPW1K, the calculated effect (∼6 kcal/mol) is much greater than the ∼1 kcal/mol effect suggested by Atkinson.[26] The breaking C−H and forming O−H bond lengths in the transition state are 1.28 Å (1.25 Å) and 1.23 Å (1.23 Å) at the B3LYP (MPW1K) level of theory; these distances are more like reactants than products, but closer to products than the distances observed in the transition state for (*Z*)-**V**.

Using the MPW1K result, one obtains an isomerization rate constant of 6.0×10^3 s^{-1} at 298 K and 1 atm, much slower than the expected rate of the O_2 reaction. Let us consider this result more closely. As discussed in the Methods section, we use the MPW1K functional because it appears to be superior to B3LYP for obtaining activation barriers to H-atom transfer reactions; this conclusion was reached *after* correction for tunneling and other dynamical effects not included our calculation of the rate constant. It is interesting that, if one *ignores* tunneling, the B3LYP value of the activation barrier for the

TABLE 1: B3LYP, CBS-QB3, and MPW1K Activation Energies and Reaction Energies at 0 K (kcal/mole, including ΔZPE) for E/Z Isomerization of Hydroxy-Isoprene Adducts 1 and 4 and 1,*n* H-Shift Reactions of 1-Butoxy Radical and Hydroxyalkoxy Radicals from Isoprene

		activation energy			energy of reaction	
reaction	B3LYP/ 6-31G(d/p)[a]	B3LYP/ 6-311G(2df,2p)	MPW1K/ 6-31G(d,p)	MPW1K/ 6-311G (2df,2p)	B3LYP/ 6-31G(d/p)[a]	B3LYP/ 6-311G(2df,2p)
1 *E*→*Z*	15.7	15.5 (15.1)[c]			0.8	0.9
4 *Z*→*E*	14.0	13.8 (15.5)[c]			0.2	0.1
$CH_3CH_2CH_2CH_2O\cdot$[b] 1,5 H-shift	9.9	9.8	13.2	12.6	2.2	0.4
III 1,5 H-shift	10.1	8.5	11.9	11.5	−8.8	−13.5
(*E*)-**V** 1,5 H-shift	10.1	8.4	12.4	11.6	−9.5	−13.6
(*Z*)-**V** 1,5 H-shift	4.7	2.1	6.6	5.4	−23.0	−27.5
(*Z*)-**VI** 1,5 H-shift	5.2	2.4	6.5	5.2	−24.3	−28.7
(*E*)-**VI** 1,4 H-shift	21.7	19.9			−9.9	−14.5

[a] For alkoxy radicals **III**, **V**, and **VI**, 6-31G(d/p) refers to the 6-31G(d) basis set, for $CH_3CH_2CH_2CH_2O\cdot$ and adducts **1** and **4**, 6-31G(d/p) refers to 6-31G(d,p). [b] For 6-31G(d,p) results, refs 32 and 35. [c] Values in parentheses are from CBS-QB3.

1,5 H-shift of 1-butoxy (9.9 kcal/mol)[32,35] yields rate constants that are a good match with rate constants inferred from experiment,[26] whereas the 12.6 kcal/mol activation barrier for the same reaction, computed here with MPW1K, would imply a rate constant about 100 times too small. To approximate the tunneling correction to the 298 K rate constant of the 1,5 H-shift reactions, we use the asymmetric Eckart potential.[55,56] The ratio, Γ(T) of the quantum mechanical versus classical rate constant is given by numerical integration of eq 4

$$\Gamma(T) = \frac{\exp(V_1/k_B T)}{k_B T}\int_o^\infty \kappa(E)\exp(-E/k_B T)dE \qquad (4)$$

where κ(E) is the transmission probability. κ(E) depends sensitively on the thickness of the barrier, as represented by the imaginary frequency, ν^*, of the vibration along the reaction coordinate. Note that eq 4 is only valid for reactants at a thermal distribution of energy, which, for unimolecular reactions, corresponds to the high-pressure limit. These reactions are not in the high-pressure limit in 1 atm of air, adding another layer of approximation to this computation of the tunneling correction.

Using the B3LYP/6-31G(d,p) value of the imaginary frequency,[57] we obtained a tunneling correction of a factor of 19 for the 1,5 H-shift of 1-butoxy. This would be consistent with a true activation barrier of ~11.5 kcal/mol, close to the MPW1K value of 11.6 kcal/mol for 1-butoxy, and consistent with the expectation that B3LYP underestimates the barrier height. For the 1,5 H-shift of (*E*)-**V**, we obtain essentially the tunneling correction, 22, as we do for 1-butoxy. Note that both functionals yield higher activation barriers for the 1,5 H-shift of 1-butoxy (by 1−1.6 kcal/mol) than those calculated for (*E*)-**V**. Now consider that the *relative rate* of 1,5 H-shift versus O_2 reaction for 1-butoxy radical, itself, is 3.3 at 298 K and 1 atm of air,[26] and that the 298 K *rate constant* for the 1,5 H-shift of (*E*)-**V** appears to be 5−10 times faster than that of 1-butoxy (due to the difference in activation barriers, since the effect of tunneling affects appears to be very similar). We conclude that the fate of the (E) isomer of **V** is dominated by the 1,5 H-shift reaction, assuming, of course, that the rate constant for the O_2 reaction is not much larger for (*E*)-**V** than it is for 1-butoxy.

The Arrhenius preexponential factors (A-factor) for the 1,5 H-shifts exhibit some interesting patterns. For **III** and (*E*)-**V**, the A-factors in the high-pressure limit are 8.0×10^{11} s^{-1} and 2.0×10^{12} s^{-1}, respectively, in reasonable accord with the 1-butoxy value of 2.3×10^{12} s^{-1} from Somnitz and Zellner.[58] However, for the (Z) isomers of both **V** and **VI**, the A-factors are an order of magnitude higher (1.6×10^{13} s^{-1}). We verified for (*Z*)-**V** that the calculated A-factor does not vary enormously (<15%) if the B3LYP/6-31G(d) values of vibrational frequencies and rotational constants are used in place of the MPW1K/6-31G(d,p) values. These high A-factors can be rationalized by the fact that intramolecular hydrogen bonding (see Figure 5) lowers the entropy of the (Z) isomers relative to **III** or (*E*)-**V** by about 20 cal/(mole K), resulting in a very small entropy difference between transition state and reactant for the (Z) isomers.

The structure of the (E) isomer of **VI** does not permit a 1,5 H-shift to occur, but we should consider the potential for a 1,4 H-shift. Such a reaction is unlikely to occur from a vinylic site (carbon 3 of the isoprene backbone), but abstraction from the methyl group (to form an allylic radical) might be feasible. However, this pathway turns out to possess a barrier of nearly 20 kcal/mol, even higher than found or suggested for other 1,4 H-shift reactions.[32,33,37] As the decomposition reaction of **VI** is slow,[10,14] the fate of the (E) isomer of **VI** is confirmed to be reaction with O_2.

Consequences for Modeling Isoprene Chemistry. Paulson and Seinfeld[19] assumed formation of a 50:50 mixture of the (E) and (Z) forms of the hydroxyalkyl radicals **1** and **4**, and their scheme is the basis of chemical mechanisms of isoprene chemistry used to model air pollution.[20] Although this appears very reasonable for **1**, it may not be valid for adduct **4**. The potential consequences of the present results for the production of ground-level ozone can only be understood through a detailed study of how the chemistry after the reactions of the (E) and (Z) isomers of the alkoxy radicals affects the total number of $NO \rightarrow NO_2$ conversions that result. We presents a qualitative discussion below for the (E) and (Z) isomers of **VI**, whose relative production is rather uncertain. A quantitative determination of these effects would require us to possess information, listed below, that is not available.

As shown in Figure 6, the (E) isomer of alkoxy radical **VI** reacts with O_2 to form HO_2. The chemistry of the (Z) isomer is more complicated. The product of its 1,5 H-shift is an allylic radical with two potential reaction pathways (for which the branching ratios are not known). One pathway leads to a MW = 100 product (of the type observed by Kwok et al.[59]) plus HO_2; the atmospheric consequences of this pathway are the same as those of the O_2 reaction of (*E*)-**VI**. However, the other pathway for (*Z*)-**VI** is expected[19,20] to lead to formation of a peroxy radical (not shown) and then, via a $NO \rightarrow NO_2$ conversion, to the alkoxy radical labeled **IX**O in Figure 4. The expected decomposition of **IX**O forms the CH_2OH radical, which will react with O_2 to form HO_2 (+ $H_2C{=}O$). The fate of the HO_2 radical is as follows

$$HO_2 + NO \rightarrow OH + NO_2 \qquad (5)$$

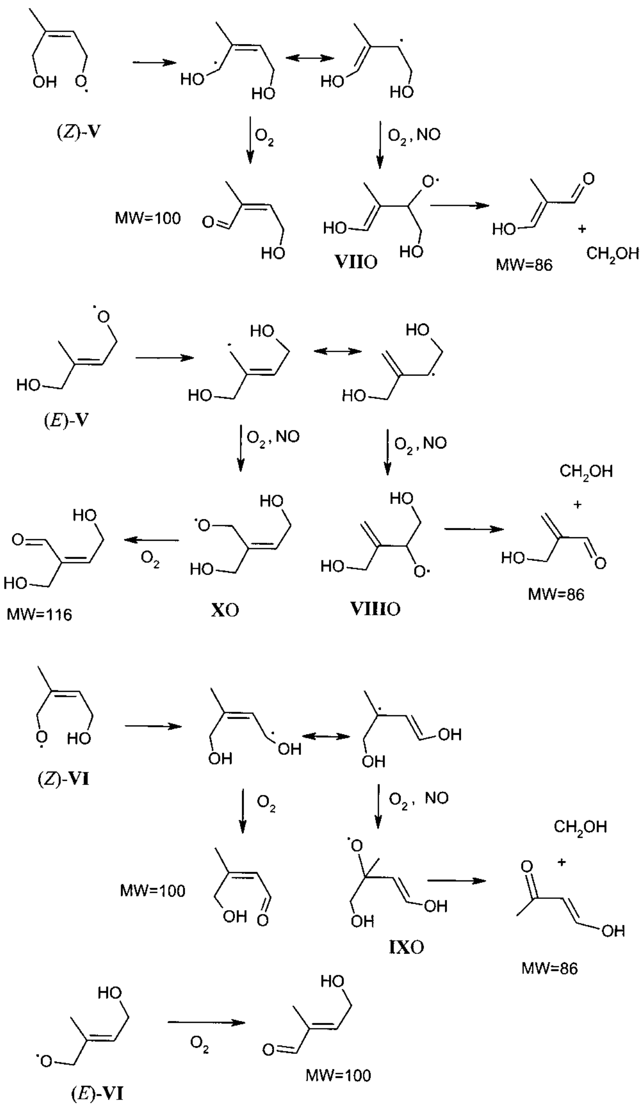

Figure 6. Predicted routes for formation of stable products following isomerization and/or O_2 reactions of (E) and (Z) isomers of alkoxy radicals **V** and **VI**. The conversion of alkyl radical R to alkoxy radical RO, depicted as one step in the Figure, is the result of the consecutive reactions: $R + O_2 \rightarrow RO_2$ followed by $RO_2 + NO \rightarrow RO + NO_2$. Stable products with molecular weights 86 and 100 of the type that have been observed in mass spectrometry experiments (ref 7 and 38) are labeled MW = 86 and MW = 100, respectively.

The reaction pathway of (*Z*)-**VI** that leads to **IX**O produces two $NO \rightarrow NO_2$ conversions, whereas the other pathway produces only one. On average, more than one $NO \rightarrow NO_2$ conversion occurs for each molecule of (*Z*)-**VI** formed, whereas only one $NO \rightarrow NO_2$ conversion follows the formation of (*E*)-**VI**. The conversion of NO to NO_2 leads to ozone formation via

$$NO_2 + h\nu \rightarrow NO + O \tag{6}$$

$$O + O_2 \rightarrow O_3 \tag{7}$$

Therefore, the uncertainty in the E/Z branching ratio for **VI** leads to uncertainty in the ozone yields from the OH-initiated degradation of isoprene.

Paulson and Seinfeld[19] also assumed that the (E) isomer of **V** would undergo the 1,5 H-shift reaction, which implies (by arguments analogous to those above) the potential for formation of more than one molecule of ozone per molecule of **V**. The O_2 reaction only has the potential to lead to the formation of one molecule of ozone. Our calculations suggest the O_2 reaction may be nonnegligible, in which case the actual number of $NO \rightarrow NO_2$ conversions per molecule of **V** would be fewer than predicted.

Quantification of these effects would require a more reliable determination of the branching ratio for formation of the (E) and (Z) isomers of **4**, of the branching ratios for the two sites of O_2 reaction with the allylic products of the 1,5 H-shift reactions of the alkoxy radicals (*Z*)-**V**, (*E*)-**V**, and (*Z*)-**VI**, as well as a better understanding of the competition between the 1,5 H-shift and O_2 reactions of (*E*)-**V**. The magnitude of the resulting uncertainties in ozone yields are significant but may not be enormous, because the branching ratios for the formation of radicals **V** and **VI** (for the (E) and (Z) forms combined) starting from OH + isoprene are only about 0.20 and 0.07[11,15] (or 0.13 and 0.11),[19] respectively. Note that the discussion above only treated rapid ozone formation resulting from organic radical chemistry; we have not considered potential ozone production over a period of hours to days due to the degradation of stable carbonyl compounds (whose atmospheric chemistry is poorly known).

Conclusions

The formation of significant yields of both (E) and (Z) isomers of isoprene-OH adducts **1** and **4**, suggested by Paulson and Seinfeld, is confirmed by our work, although our calculations yield a large uncertainty in the E/Z ratio of **4**. However, the formation of the (Z) isomer of **1** and the (E) isomer of **4** occur only via the prompt isomerization of the chemically activated adducts, because the adducts react with O_2 much faster than the thermal (E) $\rightleftarrows$ (Z) reactions can approach equilibrium. The fates of the δ-hydroxyalkoxy radicals **V** and **VI** appear to be as anticipated by Paulson and Seinfeld, except that the (*Z*) isomer of **V** may undergo some reaction with O_2 in competition with the 1,5 H-shift. These results highlight the uncertainties present in current model assumptions about branching ratios and mechanisms for the OH-initiated degradation of isoprene.

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Supporting Information Available: Cartesian coordinates of all species at B3LYP/6-311G(2df,2p) and absolute energies, including zero-point energies, of all species at all levels of theory employed. This material is available free of charge via the Internet at http://pubs.acs.org.

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