J. Am. Chem. Soc. **2001,** *123,* 4228−4234

Reactions of the Alkoxy Radicals Formed Following OH-Addition to α-Pinene and *β*-Pinene. C−C Bond Scission Reactions

Theodore S. Dibble*

Contribution from the Department of Chemistry, State University of New York-Environmental Science and Forestry, 1 Forestry Drive, Syracuse, New York 13210

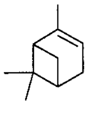
Received September 29, 2000

Abstract: The atmospheric degradation pathways of the atmospherically important terpenes α-pinene and *β*-pinene are studied using density functional theory. We employ the correlation functional of Lee, Yang, and Parr and the three-parameter HF exchange functional of Becke (B3LYP) together with the 6-31G(d) basis set. The C−C bond scission reactions of the *β*-hydroxyalkoxy radicals that are formed after OH addition to α-pinene and *β*-pinene are investigated. Both of the alkoxy radicals formed from the α-pinene−OH adduct possess a single favored C−C scission pathway with an extremely low barrier (∼3 kcal/mol) leading to the formation of pinonaldehyde. Neither of these pathways produces formaldehyde, and preliminary computational results offer some support for suggestions that 1,5 or 1,6 H-shift (isomerization) reactions of alkoxy radicals contribute to formaldehyde production. In the case of the alkoxy radical formed following OH addition to the methylene group of *β*-pinene, there exists two C−C scission reactions with nearly identical barrier heights (∼7.5 kcal/mol); one leads to known products (nopinone and formaldehyde) but the ultimate products of the competing reaction are unknown. The single C−C scission pathway of the other alkoxy radical from *β*-pinene possesses a very low (∼4 kcal/mol) barrier. The kinetically favored C−C scission reactions of all four alkoxy radicals appear to be far faster than expected rates of reaction with O_2. The rearrangement of the α-pinene−OH adduct, a key step in the proposed mechanism of formation of acetone from α-pinene, is determined to possess a barrier of 11.6 kcal/mol. This value is consistent with another computational result and is broadly consistent with the modest acetone yields observed in product yield studies.

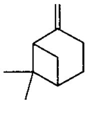
I. Introduction

On a global basis, monoterpenes ($C_{10}H_{16}$) constitute about 10% of the mass of nonmethane organic compounds (NMOCs) emitted into the atmosphere.[1] Terpenes contribute significantly to the formation of fine organic aerosols, such as those whose light-scattering properties gave rise to the names Blue Ridge and Smoky for two mountain ranges in the eastern United States.[2] Such aerosols are commonly a health hazard and may influence the formation of cloud droplets.[3] Obviously, terpenes are among the more important NMOCs for ozone and aerosol production in the lower atmosphere, and it is important to investigate their degradation pathways.

α-Pinene and *β*-pinene, whose structures depicted below, are believed to be the two most abundantly emitted terpenes in North America.[4]



α-pinene



β-pinene

During daylight hours their degradation is initiated primarily by OH radical addition to the double bond.[5] A number of papers have analyzed the stable products of the OH-initiated degradation of α- and *β*-pinene in environmental chambers,[6−13] and many of these articles have attempted to construct reaction mechanisms. Reviews of this topic have also appeared.[5,14] However, chamber studies have yet to identify, let alone quantify, many of the stable species produced in the degradation of any terpene. Even if all significant products could be identified and quantified, it would not necessarily be possible to construct a *unique* mechanism for the degradation pathways. The experimental work of Noziere, Barnes, and Becker[12] and the computational work of Vereecken and Peeters,[15,16] both on

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* Author e-mail: tsdibble@syr.edu.

[1] Guenther, A.; Hewitt, C. N.; Erickson, D.; Fall, R.; Geron, C.; Graedel, T.; Harley, P.; Klinger, L.; Lerdau, M.; McKay, W. A.; Pierce, T.; Scholes, B.; Steinbrecher, R.; Tallamraju, R.; Taylor, J.; Zimmerman, P. *J. Geophys. Res.* **1995**, *100*, 8873.

[2] Went, F. W. *Nature* **1960**, *187*, 641.

[3] Cruz, C. N.; Pandis, S. N. *Atmos. Environ.* **1997**, *31*, 2205.

[4] Guenther, A.; Geron, C.; Pierce, T.; Lamb, B.; Harley, P.; Fall, R. *Atmos. Environ.* **2000**, *34*, 2205.

[5] Atkinson, R.; Arey, J. *Acc. Chem. Res.* **1998**, *31*, 574.

[6] Arey, J.; Atkinson, R.; Aschmann, S. M. *J. Geophys. Res., D* **1990**, *95*, 18, 539.

[7] Hatakeyama, S.; Izumi, K.; Fukuyama, T.; Akimoto, H.; Washida, N. *J. Geophys. Res., D* **1991**, *96*, 947.

[8] Hakola, H.; Arey, J.; Aschmann, S. M.; Atkinson, R. *J. Atmos. Chem.* **1994**, *18*, 75.

[9] Aschmann, S. M.; Reissell, A.; Atkinson, R.; Arey, J. *J. Geophys. Res.* **1998**, *103*, 25553.

[10] Nozière, B.; Becker, K.-H. *J. Geophys. Res.* **1998**, *103*, 25587.

[11] Reissell, A.; Harry, C.; Aschmann, S. M.; Atkinson, R.; Arey, J. *J. Geophys. Res.* **1999**, *104* 13869.

[12] Nozière, B.; Barnes, I.; Becker, K.-H. *J. Geophys. Res.* **1999**, *104*, 23645.

[13] Orlando, J. J.; Noziere, B.; Tyndall, G. S.; Orzechowska, G. E.; Paulson, S. E.; Rudich, Y. *J. Geophys. Res.* **2000**, *105*, 11561.

[14] Calogirou, A.; Larsen, B. R.; Kotzias, D. *Atmos. Environ.* **1999**, *33*, 1423.

[15] Vereecken, L.; Peeters, J. *J. Phys. Chem. A* **2000**, *104*, 11140.

[16] Vereecken, L.; Peeters, J. Proceedings of EC/EUROTRAC-2 Joint Workshop, EPFL-Lausanne, Sept. 2000, in press.

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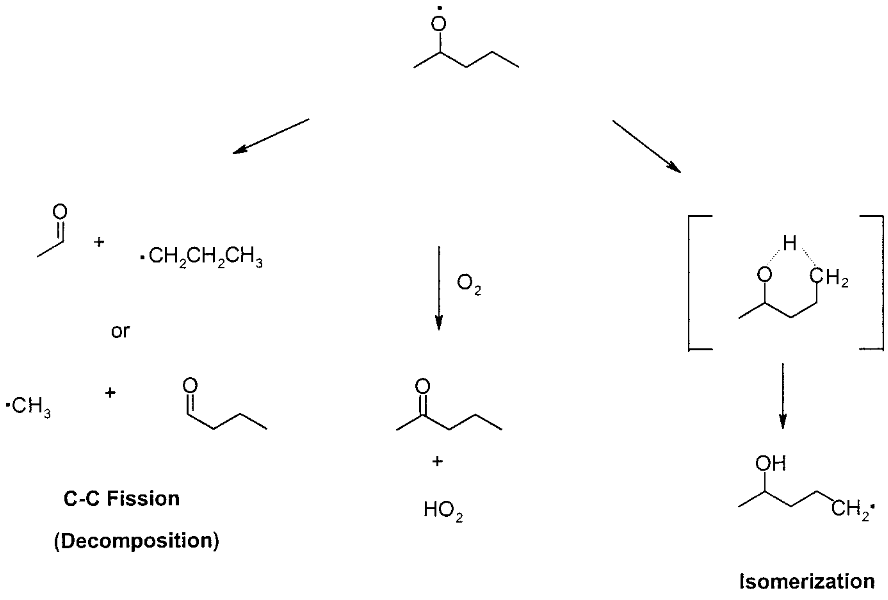
Scheme 1



α-pinene, constitute the only attempts made to quantify the branching ratios for the major reaction pathways of any terpene.

This study of α- and *β*-pinene focuses on the *β*-hydroxyalkoxy radicals, which are a major branching point in the degradation of unsaturated NMOCs, generally. The degradation of the pinenes, like that of other alkenes, is initiated primarily by radical addition (eq 1) followed by addition of molecular oxygen (eq 2) to form a peroxy radical. The peroxy radicals can produce *β*-hydroxyalkoxy radicals by two different routes (eqs 3 or 4):

$$>C{=}C< + OH \rightarrow >C(OH)C^{\bullet}< \tag{1}$$

$$>C(OH)C^{\bullet}< + O_2 \rightarrow >C(OH)C(OO^{\bullet})< \tag{2}$$

$$>C(OH)C(OO^{\bullet})< + RO_2 \rightarrow >C(OH)C(O^{\bullet})< + RO + O_2 \tag{3a}$$

$$\rightarrow \text{Other products} \tag{3b}$$

$$>C(OH)C(OO^{\bullet})< + NO \rightarrow >C(OH)C(O^{\bullet})< + NO_2 \tag{4a}$$

$$\rightarrow >C(OH)C(ONO_2)< \tag{4b}$$

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.[17]

Rate constants for the O_2 reaction of alkoxy radicals derived from small ($<C_4$) alkanes are known by direct measurement. Alkoxy radicals formed from larger alkanes have been studied primarily by indirect, albeit real-time, measurements,[18,19] although progress is being made in direct studies of these radicals, in some cases.[20] The rate of reaction with O_2 is typically $k_{298} \sim 6-10 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} (see, however, reference [21]).[17,18] In 1 atm of air, this corresponds to a pseudo-first-order rate constant of $3-5 \times 10^4$ s^{-1}. In one study to date, the presence of a *β*-hydroxy group had little affect on the rate constant.[22] By contrast, the rates of the isomerization and decomposition reactions depend enormously on structure. In acyclic alkoxy radicals, the isomerization reaction proceeds readily only if the transition state can form a six-membered ring (the 1,5 H-shift shown in Scheme 1); where this is feasible, the isomerization reaction is about an order of magnitude faster than the O_2 reaction.[17] Atkinson has developed rules for estimating substituent effects on the rate constant.[17] The 1,4 and 1,6 H-shift are slowed by strain energy[23,24] and entropy[25] considerations, respectively. In cyclohexoxy, the 1,5 H-shift in is slow because of the need to adopt a high-energy boat conformation,[26−28] but there is some computational[25] and experimental evidence[29] for the feasibility of a 1,6 H-shift in cyclic systems. For the decomposition reaction, pre-exponential factors in transition state theory at 1 atm are about 2×10^{13} s^{-1}.[30,31] A structure−activity relationship, suggested by Choo and Benson[32] and modified by Atkinson,[17] works reasonably well in reproducing the Arrhenius activation barrier (E_a) in acyclic alkoxy radicals derived from alkanes, but the validity of this approach was been challenged in the recent work of Somnitz and Zellner.[33]

Atkinson's model does not perform nearly as well for *β*-hydroxyalkoxy radicals derived from alkenes.[17] Although

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[17] Atkinson, R. *Int. J. Chem. Kinet.* **1997**, *29*, 99.

[18] Hein, H.; Hoffmann, A.; Zellner, R. *Ber. Bunsen-Ges. Phys. Chem.* **1998**, *102*, 1840, and references therein.

[19] Hein, H.; Somnitz, H.; Hoffman, A.; Zellner, R. *Z. Phys. Chem.* **2000**, *214*, 449.

[20] Deng, W.; Wang, C.; Katz, D. R.; Gawinski, G. R.; Davis, A. J.; Dibble, T. S. *Chem. Phys. Lett.* **2000**, *330*, 541.

[21] See, however, proposed modifications to the model for O_2 reaction rates of alkoxy radicals with ether linkages at the α carbon, in Aschmann, S. M.; Atkinson, R. *Int. J. Chem. Kinet.* **1999**, *31*, 501.

[22] Orlando, J. J.; Tyndall, G. S.; Bilde, M.; Ferronato, C.; Wallington, T. J.; Vereecken, L.; Peeters, J. *J. Phys. Chem. A* **1998**, *102*, 8116.

[23] Baldwin, A. C.; Barker, J. R.; Golden, D. M.; Hendry, D. G. *J. Phys. Chem.* **1977**, *81*, 2483.

[24] Lendvay, G.; Viskolcz, B. *J. Phys. Chem. A* **1998**, *102*, 10777.

[25] Dorigo, A. E.; Houk, K. N. *J. Org. Chem.* **1988**, *53*, 1650.

[26] Aschmann, S. M.; Chew, A. A.; Arey, J.; Atkinson, R. *J. Phys. Chem. A* **1997**, *101*, 8042.

[27] Platz, J.; Sehested, J.; Nielsen, O. J. *J. Phys. Chem. A* **1999**, *103* 2688.

[28] Orlando, J. J.; Iraci, L. T.; Tyndall, G. S. *J. Phys. Chem. A.* **2000**, *104*, 5072.

[29] Brum, P.; Waegall, B. In *Reactive Intermediates*; Abramowitch, R. A., Ed.; Plenum: New York, 1983; Vol. 3, p 378.

[30] Vereecken, L.; Peeters, J. *J. Phys. Chem A* **1999**, *103*, 1768.

[31] Jungkamp, T. P. W.; Smith, J. N.; Seinfeld, J. H. *J. Phys. Chem. A* **1997**, *101*, 4392.

[32] Choo, K. Y.; Benson, S. W. *Int. J. Chem. Kinet.* **1981**, *13*, 833.

[33] Somnitz, H.; Zellner, R. *Phys. Chem. Chem. Phys.* **2000**, *2*, 4319.

progress is being made, in our laboratory and elsewhere, in obtaining laser-induced fluorescence spectra of C_4 and C_5 alkoxy radicals for use in direct kinetic studies,[34−40] it may be difficult to extend the experiments to the more complicated alkoxy radicals considered herein. Presently, quantum chemical methods offer the best means to elucidate the detailed mechanisms of terpene degradation. In this paper, we employ density functional theory (DFT) methods to determine the likelihood of various C−C bond scission reactions of alkoxy radicals formed following OH addition to α-pinene and *β*-pinene. The B3LYP functional and the 6-31G(d) basis set are used throughout; activation barriers for the reactions of radicals from α-pinene are also computed using the BLYP functional. The formation of most of the identified products of α- and *β*-pinene degradation has been explained by the C−C scission reactions of the alkoxy radicals. Therefore, this paper serves to check the validity of most of the mechanisms proposed to date. Although isomerization reactions have been proposed to explain the formation of formaldehyde from α-pinene, these reactions and the subsequent chemistry have yet to be considered in detail.

Acetone is minor product of the degradation of α- and *β*-pinene,[9,11−13] but it is important because it represents a potentially significant source of HO_x radicals in the troposphere. Of the mechanisms proposed[9,13,41] to explain acetone formation from α-pinene, one, invoking rearrangement of the α-pinene−OH adduct[41] (Figure 1), has recently received support from a computational study by Vereecken and Peeters.[15,16] We have also studied this reaction, employing both the B3LYP and BLYP/6-31G(d) levels of theory.

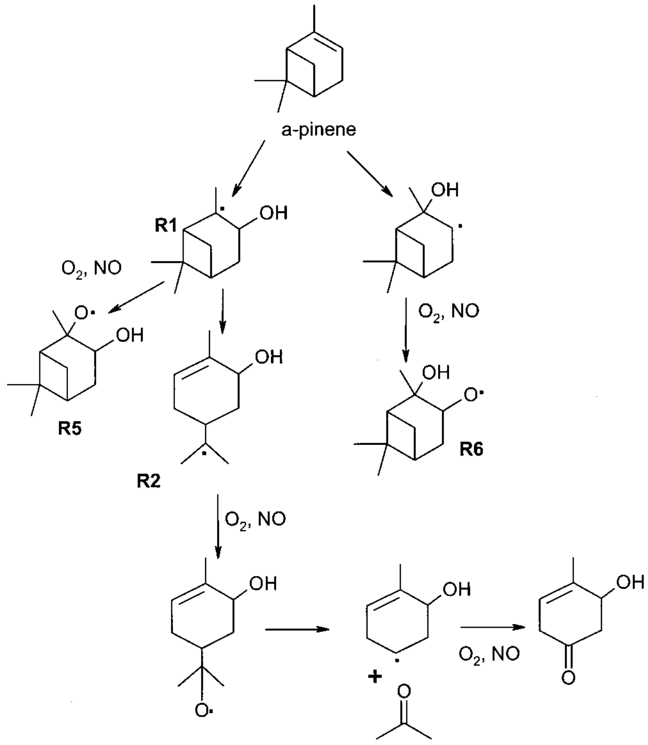

Figure 1. Mechanism for formation of alkoxy radicals from α-pinene in polluted air, and proposed mechanism for formation of acetone. In this and other figures, reaction 2 and 4a are represented as one process, and the products of 4b are omitted for clarity.

II. Computational Methods

Molecular mechanics calculations were carried out using SPARTAN[42] to obtain initial geometries of the reactants and products, and the GAUSSIAN94[43] and GAUSSIAN98[44] series of programs were used for density functional theory (DFT) calculations. The unrestricted Hartree−Fock (UHF) formulation was employed for all radicals. DFT calculations used the correlation functional of Lee, Yang, and Parr,[45] and either the three-parameter HF exchange functional of Becke[46] (B3LYP) or the exchange functional of Becke[47] (BLYP). A 6-31G(d) basis set was used throughout. Previous work has shown that calculations at the B3LYP/6-31G(d) or 6-31G(d,p) levels of theory produce highly accurate activation barriers for alkoxy radical decomposition reactions, often within 1 kcal/mol of the best value of the critical barrier height.[30,31,48,49] Use of B3LYP with larger basis sets tends to lead to underestimation of the barriers.[31,48,50] The accuracy of BLYP has not been validated for alkoxy radical reactions, but the consistency of activation energies between BLYP and B3LYP provides at least a check of consistency.

For the study of the C−C bond scission reactions of alkoxy radicals, it is not necessary to ensure that the lowest energy conformer is used, because computed activation barriers are nearly independent of the conformer chosen.[30,51] We presume the same to be true of the alkyl radical reaction studied here. The alkoxy radicals were assumed to possess an intramolecular hydrogen bond from the hydroxyl group to the radical center; this motif has been found to be the most stable for a number of other *β*-hydroxyalkoxy radicals.[30,48,49,51] The geometries of all species were optimized at the B3LYP/6-31G(d) level 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. Harmonic vibrational frequencies were calculated at the B3LYP/6-31G(d) level to verify the nature of the potential energy minima and transition states, and they were used without scaling to

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(34) Blitz, M.; Pilling, M. J.; Robertson, S. H.; Seakins, P. W. *Phys. Chem. Chem. Phys.* **1999**, *1*, 73.

(35) Wang, C.; Shemesh, L. G.; Deng, W.; Lilien, M. D.; Dibble, T. S. *J. Phys. Chem.* **1999**, *103*, 8207.

(36) Wang, C.; Deng, W.; Shemesh, L. G.; Lilien, M. D.; Katz, D. R.; Dibble, T. S. *J. Phys. Chem.* **2000**, *104*, 10368.

(37) Fittschen, C.; Hippler, H.; Viskolz, B. *Phys. Chem. Chem. Phys.* **2000**, *2*, 1677.

(38) Lotz, Ch.; Zellner, R. *Phys. Chem. Chem. Phys.* **2000**, *2*, 2353.

(39) Carter, C. C.; Atwell, J. R.; Gopalakrishnam, S.; Miller, T. A. *J. Phys. Chem. A.* **2000**, *104*, 9165.

(40) Carter, C. C.; Gopalakrishnam, S.; Miller, T. A. *J. Phys. Chem. A.*, in press.

(41) Vinckier, C.; Compernolle, F.; Saleh, A. M. *Bull. Soc. Chim. Belg.* **1997**, *106*, 501.

(42) Spartan 4.0, Wavefunction Inc. 18401 Von Karman Avenue, Suite 370, Irvine, CA 92612 U.S.A.

(43) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; 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. *Gaussian 94*, revision D.3; Gaussian, Inc.: Pittsburgh, PA, 1995.

(44) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.6; Gaussian, Inc.: Pittsburgh, PA, 1998.

(45) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(46) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(47) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(48) Dibble, T. S. *J. Phys. Chem.* **1999**, *103*, 8559.

(49) Dibble, T. S. *Chem. Phys. Lett.* **1999**, *301*, 297.

(50) Somnitz, H.; Zellner, R. *Phys. Chem. Chem. Phys.* **2000**, *2*, 1899.

(51) Vereecken, L.; Peeters, J.; Orlando, J. J.; Tyndall, G. S.; Ferronato, C. *J. Phys. Chem. A* **1999**, *103*, 4693.

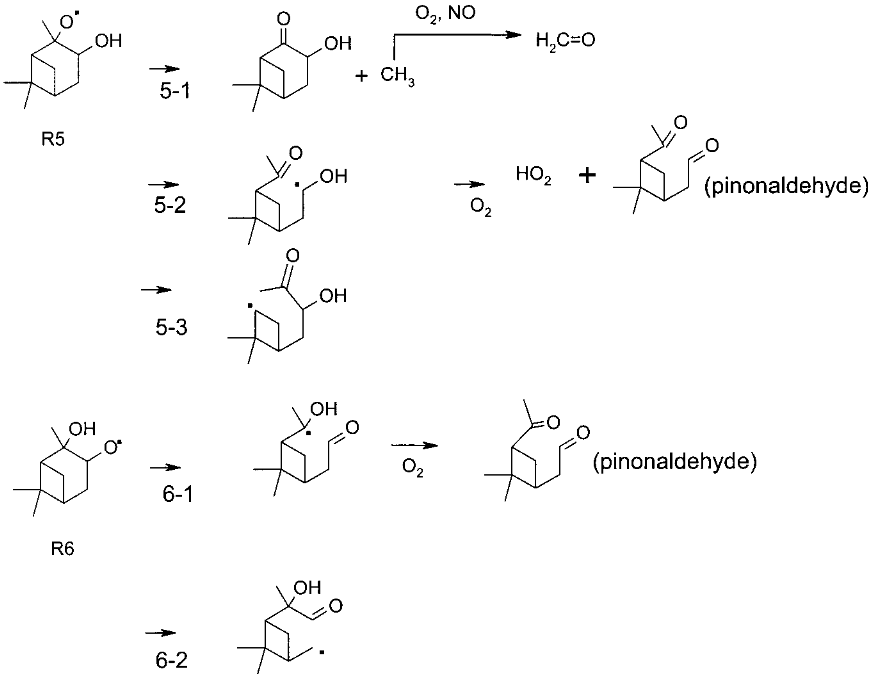

Figure 2. C−C Scission pathways for the alkoxy radicals initially formed following OH addition to α-pinene.

calculate zero point energies (ZPE). As a check of the validity of the computed activation barriers, the reactants and transition states for all of the reactions of the radicals from α-pinene were also calculated at the BLYP/6-31G(d) level of theory. All relative energies are reported as B3LYP/6-31G(d) + Δ(ZPE) values, unless otherwise noted.

III. Results and Discussion

For radicals derived from α-pinene, we adopt the identification system of Noziere, Barnes, and Becker to facilitate comparison with their results; for the radicals from β-pinene we employ Roman numerals. Reactions are identified by the reacting radical followed by a second number; i.e., 5−1 is the first reaction of radical **R5**.

We discuss the structures of these species only briefly. Alkoxy radical structures with intramolecular hydrogen bonds were obtained. Radicals **R5**, **R6**, and **II** all had H-bond distances of ~1.9 Å. The H-bonds in the transition states ranged from about 1.9−2.1 Å. Oddly, The H-bond distance in **I** was 2.2 Å, it became shorter in two transition states (2.1 Å in [I−1] and 2.0 Å in [I−3]), and much longer in one (2.64 Å in [I−2]). The distance of the breaking C−C bonds in the transition states ranged from 1.9 to 2.2 Å and was modestly correlated with activation barrier ($r^2 = 0.67$).

Let us consider the rearrangement of the α-pinene−OH adduct **R1**. As listed in Table 1, we computed an activation barrier of 11.6 kcal/mol, or 8.2 kcal/mol at BLYP. Assuming a typical Arrhenius prefactor of about 10^{13} s^{-1}, one arrives at rates of 3×10^4 s^{-1} from B3LYP or 10^7 s^{-1} from BLYP. The addition of O_2 to the alkyl radical (eq 2), with a typical rate constant of $\sim 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, should proceed with a rate of $\sim 2 \times 10^7$ s^{-1} in 1 atm of air. The computed results are broadly consistent with the conclusions of Noziere, Barnes, and Becker, that the rearrangement of **R1** to **R2** occurs 10% of the time and that the O_2 reaction occurs 90% of the time. Vereecken and Peeters[15] validated their B3LYP/6-31G(d,p) approach against the ring opening reaction in the cyclobutylmethyl radical;[52] their results suggest that B3LYP should be very reliable for this problem. According to their analysis of the B3LYP results, only the prompt rearrangement of the hot radicals can occur; if the BLYP result were correct the thermal reaction might be competitive. We note that the spin contamination of the transition state, while not high by the standards used to judge ab initio Hartree−Fock calculations, is somewhat high for a DFT calculation. Ignatyev et al., in a study of the unimolecular reactions of the ethylperoxy radical, suggested that relatively small spin contamination in B3LYP wave functions causes computed activation barriers to be too large, and that this might be corrected by using BLYP instead.[53] However, recent work shows that the B3LYP/TZ2Pf activation barrier for the reaction of concern to Igatyev et al. is in excellent agreement with the CCSD(T)/TZ2Pf//TZ2P value.[54]

Table 1. Activation Energies and Reaction Energies (kcal/mole at 0 K) for C−C Scission Reactions of β-Hydroxyalkoxy Radicals from α-pinene and β-pinene

reaction	B3LYP activation energy	BLYP activation energy	B3LYP reaction energy
[R1 → R2]	11.6	8.2	−14.1
[5−1]	13.5	12.1	0.0
[5−2]	3.4	1.9	−13.0
[5−3]	10.3	8.5	−10.6
[6−1]	2.6	1.5	−11.1
[6−2]	7.1	4.8	−3.2
[I−1]	7.6	−3.9	−
[I−2]	12.8	−11.3	−
[I−3]	7.4	−10.2	−
[II−1]	4.3	3.0	−

Activation barriers and reaction energies for all of the alkoxy radical reactions are also listed in Table 1. Computed activation barriers at BLYP are quite consistent with the B3LYP values, indicating that the computations can be regarded as reliable. As depicted in Figure 2, alkoxy radical **R5** has three potential C−C scission pathways. The one which removes the methyl group while keeping the six-membered ring intact, 5−1, has

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(52) Newcomb, M. *Tetrahedron* **1993**, *49*, 1151.

(53) Ignatyev, I. S.; Xie, Y.; Allen, W. D.; Schaefer, H. F., III *J. Chem. Phys.* **1997**, *107*, 141.

(54) Rienstra-Kiracofe, J. C.; Allen, W. D.; Schaefer, H. F., III *J. Phys. Chem.* **2000**, *104*, 9823.

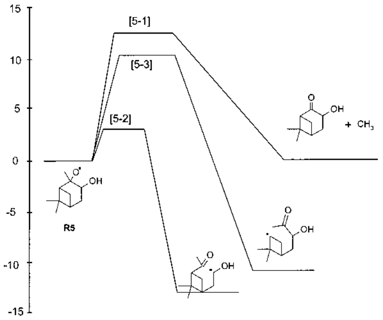

Figure 3. Potential energy profile for the C−C fission reactions of radical **R5** from α-pinene at the B3LYP/6-31G(d) + ΔZPE level of theory (energies in kcal/mole).

the largest barrier (13.5 kcal/mol). The two ring-fission reactions, 5−2 and 5−3, possess barriers of 3.4 and 10.3 kcal/mol, respectively. Reaction 5−2 leads to the formation of pinonaldehyde, which has been identified as a major product of α-pinene degradation in the presence of NO$_x$. The computed thermodynamics of these reactions follow the order of the activation barriers.

Figure 3 displays the potential energy profile for the reactions of **R5**. The results indicate that formation of the α-hydroxyalkyl radical in 5−2 is the sole unimolecular reaction pathway. In contradiction to our findings, Noziere, Barnes, and Becker suggested that reaction 5−2 occurs only 69% of the time and reaction 5−1 occurs the remaining 31% of the time; this branching ratio was invoked to explain the production of $H_2C{=}O$ in their experiments. Vereecken and Peeters have suggested that an ∼9% yield of formaldehyde can be explained by the chemistry following hydrogen abstraction by OH, occurring in competition with the expected OH addition to the double bond.[16] Even so, half or more of the formaldehyde yield remains to be explained. However, as discussed below, two alternative explanations for the formaldehyde have been offered by Aschmann et al.[9] and by Orlando et al.,[13] in terms of the isomerization of **R5** and **R6**, respectively. Using the B3LYP activation barrier to 5−2, and the typical Arrhenius pre-exponential factor of 2×10^{13} s^{-1},[17,30,31] we arrive at a rate constant on the order of 10^{10} s^{-1} at room temperature. Alkoxy radical **R5** cannot react with O_2 or undergo a 1,6 H-shift. Although **R5** has the potential to undergo a 1,5 H-shift via abstraction from one of the two methyl groups on the cyclobutane ring, the known rates of the 1,5 H-shift reaction in acyclic systems is over 10 000 times slower than the rate calculated above for 5−2. One might therefore assume that reaction 5−2 is the sole fate of **R5**. However, that conclusion would be premature. Organic chemists have long employed 1,5 H-shift reactions of alkoxy radicals in synthetic work, and in a number of cases the radical center, bound to a cyclohexane ring, abstracted a hydrogen atom from a methyl group bound to the same ring.[29,55−58] These reactions, occurring in nonpolar solvent and in competition with C−C scission reactions, often formed end-products in high yield (50−90%). Dorigo and Houk computed rate constants for some of these isomerization reactions that are competitive with the fastest decomposition rate constants computed here.[25] These facts suggest that analogous reactions could be very competitive in the gas phase.

Let us consider the 1,5 H-shift more closely. For isomers of **R5** with the radical center trans to the two methyl groups attached to the cyclobutyl ring (that is, four of the eight diastereomers), isomerization is impossible, and decomposition via 5−2 to form pinonaldehyde will be the sole fate. However, those isomers of **R5** with the radical center cis to the two methyl groups have at least the potential to undergo a 1,5 H-shift by abstracting an H-atom from those groups; Figure 4 illustrates this reaction. Aschmann et al. pointed out that this could lead to the production of formaldehyde.[9] In our preliminary work, we found activation barriers of 2.8 and 5.1 kcal/mol for the 1,5 H-shift in two different conformers of **R5** at B3LYP/6-31G-(d,p).[59] Given the uncertainties in the computed activation barriers, and in the absence of a more detailed analysis of the branching ratios for reactions leading to formaldehyde, we cannot firmly conclude that the 1,5 H-shift is a significant source of formaldehyde. Nevertheless, the process with the lower activation barrier could easily be competitive with reaction 5−2.

Turning to **R6**, we see that both decomposition reactions (Figure 2) lead to ring opening. Reaction 6−1 is favored over 6−2 by 3−4 kcal/mol in the activation barrier, implying that 6−2 is of little or no importance. From the B3LYP activation barrier of 2.6 kcal/mol for 6−1, we estimate a decomposition rate constant of $\sim 10^{11}$ s^{-1}, which is five or six orders of magnitude faster than the O_2 reaction. Noziere, Barnes, and Becker suggested that **R6** reacts exclusively via 6−1; this is consistent with our findings. The eventual product of this reaction is, again, pinonaldehyde.

In chamber studies employing gas chromatography and mass spectrometric techniques, pinonaldehyde has been detected in yields of about 30%, but FTIR methods produce yields of about 80%. The low activation barriers for **R5** and **R6** tend to support the higher value, but studies of this chemistry are far from complete. In addition to the possibility of a 1,5 H-shift for **R5**, noted above, both the 1,5 and 1,6 H-shift are plausible for certain isomers of **R6** (see Figure 4). The 1,6 H-shift of **R6**, like the 1,5 H-shift of **R5**, has been proposed [13] as an explanation for the production of formaldehyde in ∼20% yield from α-pinene. Both processes lead to the same alkoxy radical, which has the potential to react by multiple pathways, one of which generates formaldehyde. Other than the isomerization reactions, there are no obvious reactions of **R5** or **R6** leading to formaldehyde. Computational studies of the feasibility of the isomerization reactions are underway.

The alkoxy radicals derived from β-pinene and their reaction pathways are illustrated in Figure 5. Radicals **I** and **II** are predicted to follow somewhat different pathways than **R5** and **R6**. The loss of the hydroxymethyl radical from **I** via reaction I−1 to form nopinone has an activation barrier of only 7.6 kcal/mol, which is much lower than the 13.5 kcal/mol barrier to loss of the methyl radical from **R5**. The ring fission reaction leading to a cyclobutyl radical (I−2) possesses the highest activation barrier (12.8 kcal/mol). The other ring fission pathway, I−3, has an activation barrier of 7.4 kcal/mol, which is slightly lower than that of I−1 and much higher than the 3.4 kcal/mol barrier of the analogous reaction 5−2. In I−3, the lack of a hydroxy substituent at the radical center of the product raises the activation barrier over that of 5−2. The computed difference of 0.2 kcal/mol between the activation barriers of I−3 and I−1 is well within the uncertainties of the calculation. It is likely that both reactions occur to significant extents, and reaction I−3 has not previously been suggested as a significant reaction pathway. The activation barriers imply decomposition rate constants of about 10^7 s^{-1}, 200 times faster than the O_2 reaction. The 1,5 H-shift (Figure 6) is plausible for those isomers of **I**

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(55) Partch, R. E. *J. Org. Chem.* **1963**, *28*, 276.
(56) Sneen, R. A.; Matheny, N. P. *J. Am. Chem. Soc.* **1964**, *86*, 5503.
(57) Hortmann, A. G.; Youngstrom, R. E. *J. Org. Chem.* **1969**, *34*, 3392.
(58) Gibson, T. W.; Erman, W. F. *J. Am. Chem. Soc.* **1969**, *91*, 4771.
(59) Dibble, T. S. Unpublished research.

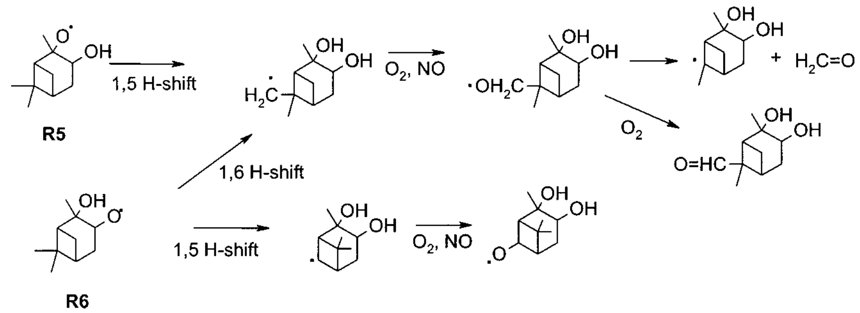

Figure 4. Potential isomerization pathways for alkoxy radicals **R5** and **R6** initially formed following OH addition to α-pinene. Isomerization reactions are feasible only for those isomers with the alkoxy radical center cis to the site of abstraction.

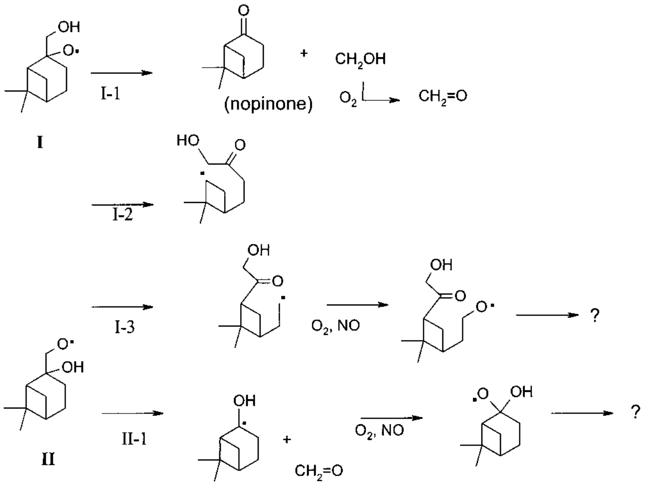

Figure 5. C−C Scission pathways for the alkoxy radicals initially formed following OH addition to *β*-pinene.

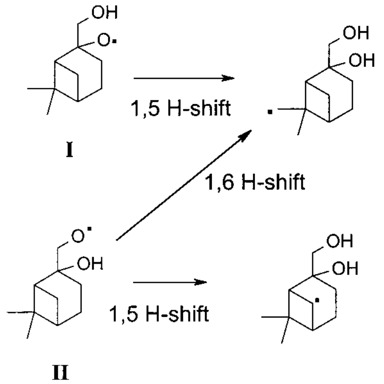

Figure 6. Potential isomerization pathways for alkoxy radicals **I** and **II** initially formed following OH addition to *β*-pinene. Isomerization reactions are feasible only for those isomers with the alkoxy radical center cis to the site of abstraction.

with the radical center cis to the two methyl groups on the cyclobutane ring. A study by Peeters et al.[60] implies that **I** and **II** are formed in a roughly 9:1 ratio, and the experimental yield of nopinone (formed only from I−1) in one study[8] is 27 ± 4%. These data suggest that reaction I−3 and/or isomerization are favored by a factor of 2.3 over I−1.

It is curious that reaction I−2 (Figure 5) is very similar to reaction 5−3 (Figure 2), yet the activation barrier to I−2 is 2.5 kcal/mol higher. We previously noted that, in [I−2], the intramolecular hydrogen bond to the radical center was much longer than in the other transition states; the breaking of this hydrogen bond could easily destabilize the transition state by ~3 kcal/mol.[30] To verify the reliability of the calculation, we recalculated the structure of **I** and [I−3] at B3LYP/6-31G(d,p), starting from a structure with a hydrogen bond length of 2.2 Å. We hypothesized that the inclusion of p functions in the basis set would lead to a more reliable treatment of the hydrogen bonding. The resulting hydrogen bond distance was only 0.01 Å longer, and the resulting activation barrier was no different than the B3LYP/6-31G(d) values.

Radical **II** possesses only one feasible decomposition pathway, the ring-retaining loss of $H_2C{=}O$. The activation barrier of 4.3 kcal/mol suggests a rate constant of 7×10^9 s^{-1}, far faster than the O_2 reaction. Those isomers of **II** with the methoxy radical substituent cis to the two methyl groups might undergo the 1,6 H-shift (to form the same radical as in the1,5 H-shift of **I**), while isomers with the $-CH_2O^{\bullet}$ groups trans to the two methyl groups could undergo a 1,5 H-shift by abstracting the hydrogen atom from the bridgehead carbon of the four-membered ring. The 1,6 H-shift (abstraction from the methylidene group at the opposite side of the ring from the radical center) would appear to be unfeasible for steric reasons.

Let us consider the atmospheric implications of this work. First, the rearrangement of **R1** to **R2** appears to be a viable pathway for formation of acetone from α-pinene. Acetone formation by this route will be accompanied by the formation of an alkoxy radical whose fate is likely to be dominated by decomposition and reaction with O_2. The favored decomposition pathways of both alkoxy radicals from α-pinene both possess very low barriers and lead to the formation of pinonaldehyde. These reactions are so fast that they rule out the occurrence of reaction with O_2, but the isomerization reactions of these radicals are yet to be studied. The occurrence of the 1,5 H-shift of **R5** and/or the 1,6 H-shift of **R6** could explain the ~20% yields of formaldehyde observed in chamber experiments. For alkoxy radical **I** formed from *β*-pinene, decomposition reactions I−1 and I−3 appear to be competitive with each other, and there is experimental support for the occurrence of I−1 (formation of nopinone) with a branching ratio of ~0.3. These reactions are calculated to be much faster than the reaction with O_2, but a 1,5 H-shift reaction is plausible for some isomers. The single feasible decomposition reaction of radical **II** is many orders of magnitude faster than the O_2 reaction, but both 1,5 and 1,6 H-shift reactions appear to be plausible.

The agreement between the BLYP and B3LYP activation barriers for reactions of **R1** and **R2** indicate that our interpretations of the relative importance of different reaction pathways are very reliable. Given the magnitude of the expected uncertainties in the activation barriers cited in Section II (and the uncertainties in the O_2 reaction rate), we would concede that reactions II−1 and II−3 may not be so fast as to eliminate the reaction of radical **II** with O_2. However, the uncertainties in

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[60] Peeters, J.; Boullart, W.; van Hoeymissen, J. In *Proc. EUROTRAC Symp. '94*; P. M. Borrell et al., Eds. PSB Academic: The Hague, Netherlands, 1994; pp 100−114.

computed activation barriers are not so large as to permit significant reaction of **R1**, **R2**, or **I** with O_2.

Reaction 4a, the major source of alkoxy radicals in the polluted atmosphere, is typically exothermic by about 15 kcal/mol; by contrast, reaction 3a, which would be the major source of alkoxy radicals in remote areas, is nearly thermoneutral. It has been shown that when small alkoxy radicals possessed of low barriers to decomposition ($\leq$ 10 kcal/mol) are formed in reaction 4a, a significant fraction are formed with sufficient internal energy to undergo prompt decomposition.[22,30,61] The large size of the radicals from the pinenes will lead to much faster quenching, but the reactions with the lowest barriers (5−2, 6−1, and II−1) may still have the potential to proceed via prompt reactions. The effect of this internal excitation is expected to enhance the rate of decomposition more than isomerization, because the Arrhenius prefactor for decomposition is thought to be much larger than that for isomerization, albeit in acyclic radicals.[17,33] Therefore, isomerization reactions, if they occur at all, might be more important for the fate of these radicals in remote areas than in urban or polluted rural environments.

What are the prospects for direct investigations of these radicals in the laboratory? The low activation barriers for decomposition of alkoxy radicals **R5**, **R6**, and **II**, combined with the potential for prompt reaction of internally hot radicals suggests that reaction 4a may not be a very good source of these radicals for direct kinetic studies. Radical **I** possesses a sufficiently high barrier to decomposition that reaction 4a might be a useful source at suitably low temperatures. As discussed elsewhere,[48] other radical sources, such as reaction 3a or photolysis of a stable precursor, are not likely to be useful for kinetic studies.

IV. Conclusions

First, the modest barrier calculated here for the rearrangement of the α-pinene−OH adduct offers support for a previously proposed mechanism of acetone formation from α-pinene. It further raises the question of whether such rearrangements are feasible for other OH−terpene adducts and suggests the need for a more thorough investigation of such reactions.

All the β-hydroxyalkoxy radicals formed from OH addition to α- and β-pinene possess sufficiently low barriers to C−C scission that they are unlikely to react with O_2 under lower tropospheric conditions. However, the results presented here for α-pinene, when combined with product yields for formaldehyde reported in previous work, strongly suggest that the decomposition reactions are not the sole fate of these radicals and that one or more isomerization reactions are important to the fate of either **R5** or **R6**. We have initiated computational studies of these reactions in order to determine which ones may be important to atmospheric chemistry. The stable products formed following reaction I−3 should be determined so experimentalists can investigate this chemistry.

Acknowledgment. The author thanks L. Vereecken, J. Peeters, and J. J. Orlando and co-workers for sharing the results of their work prior to publication, and G. Tyndall, B. Noziere, and an anonymous referee for their helpful comments. This research was supported by the National Science Foundation, under grant ATM 9712381, and by the donors of the Petroleum Research Fund, administered by the American Chemical Society, under grant 32418-G6. Further support was provided by the National Computational Science Alliance, under grant ATM-980008N, and utilized the NCSA HP-Convex Exemplar SPP-2000.

Supporting Information Available: A listing of absolute energies, zero point energies, Cartesian coordinates, and <S**2> values for all species (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA003553I

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[61] Schneider, W. F.; Wallington, T. J.; Barker, J. R.; Stahlberg, E. A. *Ber. Bunsen-Ges. Phys. Chem.* **1998**, *102*, 1850.