Competition between Reaction and Intramolecular Energy Redistribution in Solution: Observation and Nature of Nonstatistical Dynamics in the Ozonolysis of Vinyl Ethers

Larisa Mae M. Quijano and Daniel A. Singleton*

Department of Chemistry, Texas A&M University, P.O. Box 30012, College Station, Texas 77842, United States

S *Supporting Information*

ABSTRACT: Experimental product ratios in ozonolyses of alkyl vinyl ethers in solution do not fit with expectations based on statistical rate theories. The selectivity among cleavage pathways increases with the size of the alkyl group but to an extent that is far less than RRKM theory would predict. Trajectory studies account for the observed selectivities and support a mechanism involving a competition between cleavage of the primary ozonide and intramolecular vibrational energy redistribution. A statistical model is presented that assumes that RRKM theory holds for a molecular subset of the primary ozonides, allowing the rates of energy loss from the ozonides to be estimated from the observed product ratios.

Motion along a reaction coordinate is faster than either loss of energy to the medium or intramolecular vibrational energy redistribution (IVR). As a result, mechanistic intermediates are formed with excess energy, and that excess energy is to varying degrees not initially statistically distributed.[1] The governing theory for understanding the rates and selectivities of further conversions of the intermediate then depends on the time scale of those conversions. If they are slow, thermal equilibration will occur, and the rate and selectivity are predictable from transition state theory (TST). Rice–Ramsperger–Kassel–Marcus (RRKM) theory governs well the realm in which the steps following formation of an intermediate are slower than IVR but faster than or competitive with thermal equilibration, as is common in gas-phase reactions. In the fastest realm, the kinetic energy acquired during the formation of the intermediate is strongly coupled into modes that bring about its subsequent reaction faster than IVR. In such cases, experimental results (e.g., product formation selectivity) can be demonstrably inconsistent with statistical expectations,[2] but the selectivity can often be understood (at least qualitatively) by the idea of "dynamic matching." Such nonstatistical dynamic effects have been proposed to be important in many reactions.[3–7]

A middle realm in which the reaction of a mechanistic intermediate competes with IVR of the excess energy in that intermediate has long been considered.[8] Classic experiments by Doering and Rabinovitch sought to probe this competition by generating a formally symmetrical intermediate with an unsymmetrical energy distribution and then looking for product distributions betraying a lack of symmetry.[9] Alternatively, a competition between reaction and IVR has been inferred from pressure effects on product selectivity.[10] These experiments did not exclude the direct coupling of an intermediate's excess energy into its decomposition pathways; unusual rates and selectivities were assumed to arise simply from uneven distributions of molecular vibrational energy. The applicability of such experimental probes is limited,[11] and little is known about the competition between IVR and reaction in ordinary solution reactions.

We describe here a different approach to probing the competition between reaction and IVR, the importance of this competition in an ozonolysis reaction in solution and the unusual observations that result, and a simple theoretical model for understanding those observations.

The ozonolysis of alkenes is a fundamental organic reaction that is also of importance in atmospheric chemistry. The normal mechanism for these cycloadditions involves a 1,3-dipolar cycloaddition to afford a 1,2,3-trioxolane called the primary ozonide (**PO**), followed by cleavage of the **PO** to afford a carbonyl compound and a carbonyl oxide, known as the Criegee intermediate (**CI**). The combination of the high exothermicity of the cycloaddition step (>50 kcal/mol) and the low stability of the **PO**, initially saddled with that excess energy, would promote nonstatistical dynamics in the cleavage step. In fact, Hase and co-workers performed theoretical studies of the dynamics of the gas-phase ozonolysis of propene and predicted aspects of its post-transition-state dynamics to be nonstatistical.[12] We envisioned that in the right system we might be able to see substantial experimental consequences of nonstatistical dynamics on ozonolyses in solution and use the experimental observations to probe the dynamics.

We chose to study the ozonolysis of vinyl ethers because it is a well-behaved reaction that avoids some of the common complications in ozonolyses of alkenes and because the regiochemistry of the cleavage of the **PO** can be readily studied. The **PO** derived from a vinyl ether may cleave in two ways: cleavage *A*, which affords an alkyl formate (**1**) and formaldehyde oxide (**CI-***A*), or cleavage *B*, which affords a formate oxide (**CI-***B*) and formaldehyde. In methanol, the **CI**s are rapidly trapped, affording hydroperoxides **2** and **3**, and the formaldehyde is converted to its hemiacetal **4**. In ozonolysis of vinyl ethers in methanol-d_4, ^{1}H NMR peaks attributable to products **1–4** were readily identified.

Table 1. Experimental and Statistically Predicted A/B Ratios

alkyl group	exptl A/B[a,b,c] (n)	predicted A/B[d,e]	
		TST	RRKM
methyl	25.9 ± 1.2 (12)	43 × 10⁵	10.0
ethyl	36.3 ± 1.0 (33)	9.8 × 10⁵	10.9
butyl	47.2 ± 2.0 (14)	8.5 × 10⁵	18.5
octyl	54.8 ± 1.8 (16)	9.6 × 10⁵	47.8
3,7-dimethyloctyl	63.2 ± 2.0 (7)	5.7 × 10⁵	61
3,7,11,15-tetramethylhexadecyl	74.5 ± 1.9 (9)	9.6 × 10⁵	343
ethyl (−31 °C)	33.7 ± 1.3 (10)	2.4 × 10⁵	10.9
ethyl (8 °C)	24.7 ± 1.4 (10)	0.45 × 10⁵	10.9
ethyl (23 °C)	23.6 ± 2.1 (14)	0.26 × 10⁵	10.8
octyl (−31 °C)	51.5 ± 1.0 (5)	2.5 × 10⁵	47.9
octyl (8 °C)	43.1 ± 0.6 (7)	0.44 × 10⁵	48.0
octyl (23 °C)	40.0 ± 0.7 (8)	0.26 × 10⁵	48.1

[a] The ratios given are based on the ¹H NMR integration for the methine peak of **3** vs the formyl peak of **1**. [b] Uncertainties are 95% confidence ranges; the number of measurements is given in parentheses. [c] The reactions were conducted at −55 °C unless otherwise noted. [d] Gaussian-4 (G4) energetics were used for R = methyl, ethyl, and butyl. For the larger alkyl groups, the R = butyl G4 relative energies were used, and small correction factors for differences in the relative energies seen in B3LYP/GTBas3 calculations were included. [e] The two lowest-energy cleavage-A TSs and the two lowest-energy cleavage-B TSs were used in all of the calculations.

The NMR assignments were confirmed by independent syntheses (ozonolyses of ethylene and *trans*-1,2-diethoxyethylene) as well as a ²H NMR study of a reaction employing 1-deutero-1-ethoxyethylene [see the Supporting Information (SI)]. The ratio of the cleavage-A and -B products did not vary significantly with ozonolysis conversions from 20 to 100% conducted within a few minutes, though secondary reactions did occur with excess ozone or extended reaction times. The ratios of the cleavage products observed for a series of alkyl vinyl ethers are shown in Table 1.
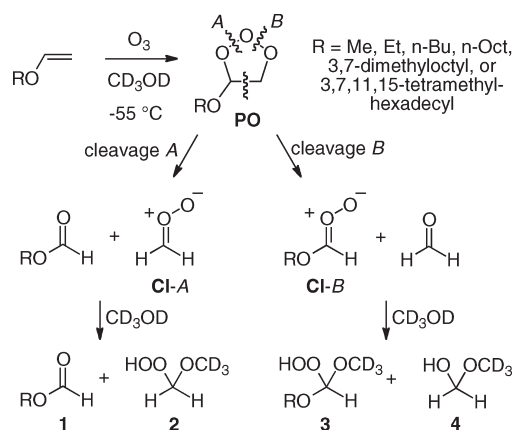
The experimental selectivities are surprising in a number of ways. The selectivity increases consistently with the size of the alkyl group, and the selectivity changes in going from R = ethyl to R = butyl or from R = butyl to R = octyl are larger than normally attributable to electronic substituent effects. The selectivity with R = 3,7,11,15-tetramethylhexadecyl is greater than that with R = 3, 7-dimethyloctyl, even though the first structural difference
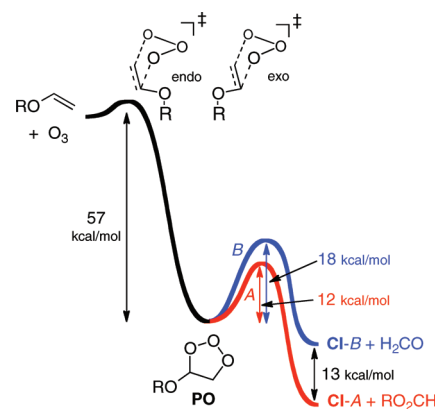

Figure 1. Approximate energy profile for the reaction of the various vinyl ethers with ozone based on G4 calculations.

between the two is 10 bonds away from a reactive center. The effect of the alkyl groups is not attributable to a medium effect; addition of pentane to the reaction mixture had no effect on the selectivity.

Another observation is that the changes in selectivity with temperature are relatively small. The observed selectivities with R = ethyl and R = octyl from −55 to 23 °C correspond to $\Delta\Delta H^{\ddagger}$ values of 0.8 and 0.5 kcal/mol, with $\Delta\Delta S^{\ddagger}$ values of −4 and −6 e.u., respectively. If $\Delta\Delta S^{\ddagger}$ were ∼0 e.u., as might be expected intuitively for the similar A and B cleavages (in the G4 calculations, it is +0.6 e.u. at −55 °C), then the selectivity would change by a factor of 2.6−2.9 instead of only 1.4−1.5 over the temperature range.

The most striking observation is that the experimental selectivities are 4−5 orders of magnitude lower than expected on the basis of TST. The energy profile for the reaction of ozone with vinyl ethers is depicted in Figure 1. Cleavage A is thermodynamically favored over cleavage B by 13.0 kcal/mol, and the calculated free-energy barriers reflect the thermodynamics, favoring cleavage A by 5.9−6.6 kcal/mol in G4 calculations (see the SI for alternative computational methods, including solvent-model calculations). If TST were applicable in this reaction, cleavage B would be unobservable.

RRKM theory comes closer to predicting the observed selectivity but fails in an important way. RRKM rate constants were calculated for the cleavage of the **PO**s, assuming that the ozone/vinyl ether cycloaddition transition states (TSs) have a canonical energy distribution and that no energy is lost in forming the **PO**s. With the resulting >57 kcal/mol of extra energy, the RRKM-predicted A/B selectivities are much lower than the TST-predicted selectivities and fall in a range similar to that for the experimental results. However, there is a substantial problem with the trend in the RRKM-predicted selectivities: the RRKM calculations predict that as the size of the alkyl group increases, the selectivity should increase greatly. This prediction is understandable because RRKM theory assumes that the distribution of molecular energy is equilibrated, allowing large alkyl groups to act as "heat sinks" for the reactions. Such a heat-sink effect would in essence cool the hot 1,2,3-trioxolane ring, causing the selectivity to rise dramatically. Experimentally, this does not happen; the increase in selectivity is much smaller than that predicted by RRKM theory.

The most economical explanation for this data is that the selectivities reflect a competition between cleavage of the **PO** ring and IVR. Larger alkyl groups can better accept the energy generated

Table 2. Trajectory Results, Projected Cleavage-B Percentages after 1 ps (%B), and Projected A/B Ratios

alkyl group	endo TS	exo TS	%B[a]	A/B[b]
methyl	A: 522	A: 1147	3.6	27
	B: 38 (1.0%)	B: 129 (2.2%)		
	no rxn: 3129	no rxn: 4470		
ethyl	A: 420	A: 1089	2.8	35
	B: 36 (0.6%)	B: 131 (2.3%)		
	no rxn: 5423	no rxn: 4445		
butyl	A: 395	A: 1075	2.2	45
	B: 24 (0.4%)	B: 119 (2.1%)		
	no rxn: 5731	no rxn: 4564		
octyl	A: 417	A: 560	1.8	55
	B: 27 (0.4%)	B: 52 (1.6%)		
	no rxn: 7136	no rxn: 2655		
3,7-dimethyloctyl	A: 258	A: 811	1.7	57
	B: 24 (0.4%)	B: 61 (1.3%)		
	no rxn: 5278	no rxn: 3872		
3,7,11,15-tetramethyl-hexadecyl	A: 265	A: 561	1.6	62
	B: 12 (0.3%)	B: 51 (1.5%)		
	no rxn: 4163	no rxn: 2709		

[a] Calculated by weighting the endo and exo results in a 74:26 ratio (based on G4 energetics) and assuming that the average rate of cleavage B observed between 200 and 500 fs continues for, on average, a total time of 1 ps (see the text). [b] Calculated as (100% − %B)/%B.

by **PO** formation, but the vibrational energy that is initially localized in the 1,2,3-trioxolane cannot be fully distributed throughout the molecule before substantial ring cleavage occurs.

To explore this idea, quasiclassical direct-dynamics trajectory calculations[13] were used to study these reactions. The trajectories were carried out on an ONIOM potential energy surface using density functional theory (DFT) for the **PO** ring and the PDDG/PM3 semiempirical method[14] for the various alkyl chains. The DFT part of the calculation employed a locally modified hybrid functional (see the SI for details) that was parametrized to approximately reproduce a known barrier for a primary ozonide cleavage as well as G4 energetics for the initial cycloaddition barrier and exothermicity. The lowest-energy endo and exo TSs (Figure 1) for the various ozone/vinyl ether cycloadditions were used as the starting point for the trajectories. Each normal mode was given its zero-point energy (ZPE) plus a Boltzmann sampling of additional energy appropriate for a temperature of −55 °C and a random phase and sign for its initial velocity. The trajectories were integrated in 1 fs steps until either ring cleavage occurred or a 500 fs time limit (to minimize nonphysical IVR of the ZPE) was reached.

The trajectory results (Table 2) provide both qualitative and quantitative support for a competition between ring cleavage and IVR. Qualitatively, the trajectories show a substantial proportion of cleavage B that falls off moderately as the size of the alkyl group increases. With R = methyl and R = ethyl, the proportion of cleavage B observed in the trajectories is very close to that predicted by the RRKM calculations. With larger alkyl groups, the proportion of cleavage B decreases but by only a factor of 2−3 for the largest group as opposed to a factor of 34 in the RRKM predictions. All of this fits with the experimental observations.

The energy generated from formation of the **PO** should undergo both IVR and loss to solvent as time goes on, and a quantitative analysis of the trajectory results requires some allowance for this cooling. As the simplest possibility, we considered a two-state model. In this model, most **PO** molecules undergo

thermal deactivation to give a "cold" state that affords only cleavage A, but the initially formed "hot" state affords either cleavage A or cleavage B at a rate that is assumed to match that given by the trajectory results in the time period between 200 and 500 fs after the cycloaddition TS. (Negligible cleavage B occurs before 200 fs into the trajectories.) From an average lifetime of the hot state, the A/B ratio can be calculated. This process is to some degree an exercise in numerology, but the lifetime of the hot state is the only adjustable parameter. When the average lifetime of the hot state is set at the seemingly reasonable value of 1 ps, the projected A/B ratios for the various vinyl ethers are in phenomenal agreement with experiment.[15]

The flow of energy from the primary ozonide ring into the alkyl groups was examined by following the kinetic energy of the atoms in the alkyl groups in the 100−500 fs time frame. The average rates of increase in the alkyl group energy for R = ethyl, R = butyl, and R = octyl (based on ∼400 trajectories in each case) were 17, 19, and 20 kcal mol^{-1} ps^{-1}, respectively. This observation suggests that the decrease in cleavage B as the alkyl group size is increased, experimentally and in the trajectories, is associated with the increasing rate at which the larger alkyl groups take up energy. However, the rate at which the octyl group absorbs energy in the trajectories within the first few hundred femtoseconds is only moderately greater than that for the ethyl group, and the selectivity change is lower than would be expected from the two groups' total ability to take up energy.

Since the trajectory results appear to reflect the experimental observations well, it is of interest to compare some of the details of the trajectory results with RRKM predictions. For this comparison, we consider only the trajectories initiated from the exo cycloaddition TS, because the endo TS leads to a **PO** conformer that must undergo conformational interconversion to access the lowest-energy cleavage TSs (see the SI for a discussion of this conformational interconversion). For the small R = methyl system, RRKM theory appears to work quite well in predicting both the rate of cleavage B (5×10^{10} s^{-1} vs ∼6×10^{10} s^{-1} in the trajectories) and the A/B ratio (10:1 vs 9:1 in the trajectories). On the other hand, for the R = tetramethylhexadecyl system, RRKM theory predictions are off by 3 orders of magnitude for the rate of cleavage B (4×10^7 s^{-1} vs ∼4×10^{10} s^{-1} in the trajectories) and a factor of 31 for the A/B ratio (343:1 vs 11:1 in the trajectories).

The success of RRKM theory for the R = methyl system suggests that cleavage B does not arise by a strong coupling of the **PO**'s initial excess energy into the cleavage pathway, as in the dynamic matching phenomenon. This idea is supported by the observation that in the trajectories there is a significant time lag between the formation of the **PO** (median time 71 fs) and the rise of cleavage-B events (>200 fs). This contrasts with the nonstatistical behavior seen in the cleavage of the acetone cation radical, where the reaction reaches a maximum rate within 50 fs and many trajectories bypass the area of the formal intermediate.[3e] The onset of cleavage within the **PO** appears to require some IVR within the ring, which takes some time, and the cleavage then proceeds nonstatistically simply by virtue of the localization of the energy within the area of the ring.

If RRKM theory may be viewed as applicable for each system within a "molecular subset" equal to the size of the R = methyl system (or, more precisely, a subset of the normal modes localized in that portion of the molecule), then an approximate statistical model can be developed to interpret our experimental observations. Following an extension of a process used previously by Rabinovitch,[10a] our model assumes that the ensemble

13826

dx.doi.org/10.1021/ja2043497 |J. Am. Chem. Soc. 2011, 133, 13824–13827

of energies E^t within the molecular subset decays exponentially from the initial ensemble of energies E^0 (eq 1) and that the rate constants $k_A(E^t)$ for cleavage A and $k_B(E^t)$ for cleavage B are those calculated from RRKM theory for the R = methyl system. The amount of cleavage B observed is then calculated using eq 2, in which $PO^*(t)$ is the amount of energetic **PO** that survives to time t [decreased by $k_A(E^t)$ and $k_B(E^t)$ processes]. The decay constant λ is then set for each reaction to the value that affords the experimental product ratio.

$$E^t = E^0 e^{-\lambda t} \tag{1}$$

$$\text{amount of cleavage } B = \int_{E^0, t} k_B(E^t)\, PO^*(t)\, dt \tag{2}$$

The λ values obtained in this way are 1.6×10^{11}, 2.5×10^{11}, 3.5×10^{11}, 4.2×10^{11}, 4.9×10^{11}, and 5.5×10^{11} s^{-1} for R = methyl, ethyl, butyl, octyl, dimethyloctyl, and tetramethylhexadecyl, respectively. These values are notably slower than IVR rate constants of 10^{12}–10^{13} s^{-1} inferred by Rabinovitch but quite consistent with directly measured IVR rate constants observed by Schwarzer.[16] These λ values also fit well with the rates of energy loss to the alkyl groups found in the trajectories studies ($\lambda = 4 \times 10^{11}$ s^{-1} corresponds to an energy loss of ~20 kcal/mol in 1 ps). The particular values of λ depend on both the applicability of the model and the accuracy of the calculated barriers,[17] so there is some danger of overinterpretation, but it is interesting that λ values for the larger alkyl groups are more than a factor of 2 greater than that for the methyl system. This suggests that most of the **PO** cooling in the larger systems is intramolecular, as would be consistent with direct observations of vibrational relaxation by Crim.[18]

When an experimental product ratio does not fit with a calculated selectivity based on theoretically calculated barriers and statistical theory, it would normally be assumed that the calculated barriers are simply inaccurate, not that statistical theory is inapplicable to a reaction. In this way, outside of the special cases of formally symmetrical intermediates, any single selectivity observation may be shoehorned into statistical rate theories. This is normally perfectly correct, but the present results show that it need not be so, even for simple reactions in solution. Our process of examining the selectivity in a homologous series of reactions should be of broader value in recognizing reactions involving nonstatistical dynamics. The physical ideas here are not new; for example, the idea that large molecules might behave like smaller molecules was suggested by Rice in 1930.[19] However, the results herein support and provide considerable insight into the impact of a fundamental physical phenomenon, the redistribution of vibrational energy in molecules, on the experimentally observed products in an ordinary organic reaction in solution.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Complete descriptions of experimental procedures and additional observations, calculations, and structures. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
singleton@mail.chem.tamu.edu

■ REFERENCES

(1) (a) Hase, W. L.; Buckowski, D. G.; Swamy, K. N. *J. Phys. Chem.* **1983**, 87, 2754. (b) Hase, W. L. *Science* **1994**, 266, 998.

(2) (a) Carpenter, B. K. *Angew. Chem., Int. Ed.* **1998**, 37, 3340. (b) Lourderaj, U.; Hase, W. L. *J. Phys. Chem. A* **2009**, 113, 2236. (c) Carpenter, B. K. *J. Phys. Org. Chem.* **2003**, 16, 858.

(3) (a) Litovitz, A.; Keresztes, I.; Carpenter, B. K. *J. Am. Chem. Soc.* **2008**, 130, 12085. (b) Carpenter, B. K. *J. Am. Chem. Soc.* **1996**, 118, 10329. (c) Sun, L.; Song, K.; Hase, W. L. *Science* **2002**, 296, 875. (d) Osterheld, T. H.; Brauman, J. I. *J. Am. Chem. Soc.* **1993**, 115, 10311. (e) Nummela, J. A.; Carpenter, B. K. *J. Am. Chem. Soc.* **2002**, 124, 8512. (f) Doubleday, C.; Suhrada, C. P.; Houk, K. N. *J. Am. Chem. Soc.* **2006**, 128, 90. (g) Doubleday, C.; Nendel, M.; Houk, K. N.; Thweatt, D.; Page, M. *J. Am. Chem. Soc.* **1999**, 121, 4720. (h) Doubleday, C., Jr.; Bolton, K.; Hase, W. L. *J. Am. Chem. Soc.* **1997**, 119, 5251.

(4) (a) Carpenter, B. K. *J. Am. Chem. Soc.* **1985**, 107, 5730. (b) Carpenter, B. K. *J. Am. Chem. Soc.* **1995**, 117, 6336. (c) Reyes, M. B.; Carpenter, B. K. *J. Am. Chem. Soc.* **2000**, 122, 10163. (d) Reyes, M. B.; Lobkovsky, E. B.; Carpenter, B. K. *J. Am. Chem. Soc.* **2002**, 124, 641.

(5) Debbert, S. L.; Carpenter, B. K.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **2002**, 124, 7896.

(6) (a) Oyola, Y.; Singleton, D. A. *J. Am. Chem. Soc.* **2009**, 131, 3130. (b) Ussing, B. R.; Hang, C.; Singleton, D. A. *J. Am. Chem. Soc.* **2006**, 128, 7594. (c) Wang, Z.; Hirschi, J. S.; Singleton, D. A. *Angew. Chem., Int. Ed.* **2009**, 48, 9156.

(7) Glowacki, D. R.; Marsden, S. P.; Pilling, M. J. *J. Am. Chem. Soc.* **2009**, 131, 13896.

(8) (a) Bunker, D. L.; Hase, W. L. *J. Chem. Phys.* **1973**, 59, 4621. (b) Oref, I.; Rabinovitch, B. S. *Acc. Chem. Res.* **1979**, 12, 166.

(9) (a) Doering, W. V. E.; Gilbert, J. C.; Leermakers, P. A. *Tetrahedron* **1968**, 24, 6863. (b) Rynbrandt, J. D.; Rabinovitch, B. S. *J. Phys. Chem.* **1971**, 75, 2164.

(10) (a) Meagher, J. F.; Chao, K. J.; Barker, J. R; Rabinovitch, B. S. *J. Phys. Chem.* **1974**, 78, 2535. (b) Ko, A.-N.; Rabinovitch, B. S. *Chem. Phys.* **1978**, 29, 271. (c) Wrigley, S. P.; Rabinovitch, B. S. *Chem. Phys. Lett.* **1983**, 95, 363.

(11) Their interpretation has also been questioned. See: Doering, W. v. E.; Ehlhardt, W. J. *J. Am. Chem. Soc.* **1987**, 109, 2697. Also see: Carpenter, B. K.; Pittner, J.; Veis, L. *J. Phys. Chem. A* **2009**, 113, 10557.

(12) Vayner, G.; Addepalli, S. V.; Song, K.; Hase, W. L. *J. Chem. Phys.* **2006**, 125, No. 014317.

(13) Hase, W. L.; Song, K. H.; Gordon, M. S. *Comput. Sci. Eng.* **2003**, 5, 36.

(14) Repasky, M. P.; Chandrasekhar, J.; Jorgensen, W. L. *J. Comput. Chem.* **2002**, 23, 1601.

(15) Recent work (see: Zheng, J.; Papajak, E.; Truhlar, D. G. *J. Am. Chem. Soc.* **2009**, 131, 15754) has proposed a "canonical competitive nonstatistical model" (CCNM) to predict product branching ratios after dynamical bottlenecks of the type seen in the current reaction. The CCNM model divides the branching into "indirect" and "direct" components, the former being predicted using TST and the latter using phase-space theory. The large barriers for the reaction of the primary ozonide in the present work cause the CCNM model to allocate 100% of the reaction to the indirect component, so the CCNM model fails qualitatively to the extent that TST itself fails.

(16) (a) Schwarzer, D.; Hanisch, C.; Kutne, P.; Troe, J. *J. Phys. Chem. A* **2002**, 106, 8019. (b) Schwarzer, D.; Kutne, P.; Schröder, C.; Troe, J. *J. Chem. Phys.* **2004**, 121, 1754.

(17) The λ values are relatively insensitive to errors in the barriers. A 2 kcal/mol decrease in the barriers for both cleavage A and cleavage B would lead to an increase in λ by a factor of ~2.2. A 2 kcal/mol decrease in the barrier for cleavage B by itself would increase λ by a factor of ~2.6.

(18) (a) Cox, M. J.; Crim, F. F. *J. Phys. Chem. A* **2005**, 109, 11673. Also see: (b) Bradford, S. *Science* **2011**, 331, 1398.

(19) Rice, O. K. *Z. Phys. Chem., Abt. B* **1930**, 7, 226.

13827

dx.doi.org/10.1021/ja2043497 |*J. Am. Chem. Soc.* 2011, 133, 13824–13827