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

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Abstract

Experimental product ratios in ozonolyses of alkyl vinyl ethers in solution do not fit with expectations from 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. An approximate statistical model is presented that assumes that RRKM theory holds for a molecular subset of the primary ozonides, allowing estimates of the rates of energy loss from the primary ozonides based on the observed product ratios.

The time scale associated with 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 is predictable from transition state theory (TST). 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 observations such as the selectivity in product formation can be demonstrably inconsistent with statistical expectations,² but the selectivity may 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.^{3,4,5,6,7}

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 Rabinovich sought to probe this competition by generating a formally symmetrical intermediate with an unsymmetrical distribution of energy, then looking for product distributions that betray a lack of actual symmetry.⁹ Alternatively, a competition between reaction and IVR has been inferred from pressure effects on product selectivity.¹⁰ These experiments do not exclude the direct coupling of an intermediate’s excess energy into its decomposition paths, but unusual rates and selectivities were assumed to arise simply from the uneven distribution of molecular vibrational energy. The applicability of

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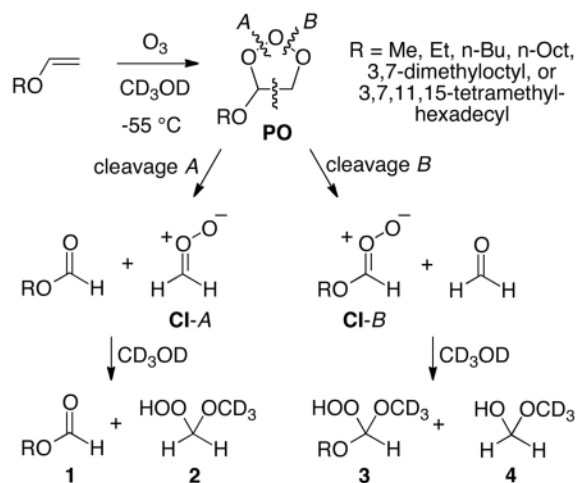
Supporting Information. Complete descriptions of experimental procedures and additional observations, calculations and structures. (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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 the reaction of an intermediate 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, the primary ozonide (**PO**), followed by cleavage of the **PO** to afford a carbonyl compound and a carbonyl oxide, the Criegee intermediate (**CI**). The combination of a high exothermicity of the cycloaddition step (>50 kcal/mol) and the low stability of the **PO**, initially saddled with that excess energy, suggests the possibility that nonstatistical dynamics could be of importance in the cleavage step. In fact, Hase and coworkers have theoretically studied the dynamics of the gas-phase ozonolysis of propene and predicted that aspects of its post-transition state dynamics are non-statistical.¹² We envisioned that in the right system we might be able to see substantial experimental consequences of non-statistical dynamics on ozonolyses in solution, and make use of the experimental observations to probe the dynamics.

We chose the ozonolysis of vinyl ethers for study 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** may be readily studied. The **PO** derived from a vinyl ether may cleave in two ways: cleavage *A*, affording an alkyl formate (**1**) and formaldehyde oxide (**CI-A**), or cleavage *B*, affording 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, ¹H NMR peaks attributable to products **1** – **4** are readily identified. The NMR assignments were confirmed by independent syntheses (ozonolyses of ethylene and of *trans*-1,2-diethoxyethylene) as well as a ²H NMR study of a reaction employing 1-deutero-1-ethoxyethylene (see the Supporting Information). The ratio of the products from cleavages *A* versus *B* does not vary significantly with ozonolysis conversions from 20 to 100% conducted within a few minutes, though secondary reactions do occur with excess ozone or extended times. The ratio of the cleavage pathways observed for a series of alkyl vinyl ethers is summarized 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 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 between the two is ten 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 selectivity changes relatively little with changes in temperature. The observed selectivities with R=ethyl and R=octyl at -55 to 23 °C correspond to phenomenological $\Delta\Delta H^\ddagger$'s of 0.8 and 0.5 kcal/mol, with $\Delta\Delta S^\ddagger$ values of -4 e.u. and -6 e.u., respectively. If $\Delta\Delta S^\ddagger$ were ≈ 0 e.u., as might be expected intuitively for the similar *A* versus *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 four to five orders of magnitude lower than expected from 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 (based on G4 calculations for the initial cleavage products from methyl vinyl ether), and calculated free-energy barriers reflect the thermodynamics, favoring cleavage *A* by 5.9 – 6.6 kcal/mol in G4 calculations (see the Supporting Information for alternative calculational methods including solvent-model calculations). If TST were applicable in this reaction, cleavage *B* would be unobservable.

RRKM theory comes much closer to predicting the observed selectivity, but then fails in an important way. RRKM rate constants were calculated for the cleavage of the **PO**s (with their various alkyl groups) 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 greatly decreased compared to the TST-predicted selectivities, falling in a range similar to the experimental results. However, there is a substantial problem with the trend in the RRKM-predicted selectivities. As the size of the alkyl group of the vinyl ether is increased, the RRKM calculations predict that the selectivity should greatly increase. 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 with the size of the alkyl group is much smaller than what RRKM theory predicts.

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 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 and obtain more detailed insight into the competition between the cleavage reaction and IVR, quasi-classical direct-dynamics trajectory calculations¹³ were used to study these reactions. The trajectories were carried out on an ONIOM potential energy surface using DFT for the **PO** ring and using the PDDG/PM3 semiempirical method¹⁴ for the various alkyl chains. The DFT part of the calculation employed a locally modified hybrid functional (see the Supporting Information for details) that was parameterized 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, giving each normal mode its ZPE plus a Boltzmann sampling of additional energy appropriate for $-55\text{ }^{\circ}\text{C}$, with a random phase and sign for its initial velocity. Employing a Verlet algorithm, 1-fs steps were taken until either ring cleavage occurred or a 500-fs time limit (to minimize non-physical IVR of the ZPE) was reached. The results are summarized in Table 2.

The trajectory results 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 is increased. With *R*=methyl and *R*=ethyl, the proportion of cleavage *B* that is observed in the trajectories is very close to that predicted from the RRKM calculations. With larger alkyl groups, cleavage *B* decreases but only by a factor of 2–3 for the largest group, as opposed to a factor of 34 expected from the RRKM predictions. All of this fits with the experimental observations.

The energy generated from the **PO** formation 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 have 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 fs and 500 fs after the cycloaddition TS. (Negligible cleavage *B* occurs before 200 fs into the trajectories.) From an average lifetime for 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 put 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 rate of increase in the alkyl-group energy for *R*=ethyl, *R*=butyl, and *R*=octyl (based on ≈ 400 trajectories in each case) was 17, 19, and 20 kcal/mol/ps, respectively. This observation suggests that the decrease in cleavage *B* as alkyl group size is increased, experimentally and in the trajectories, is associated with an 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 based on the two groups’ total ability to take up energy as reflected by the RRKM calculations.

Since the trajectory results appear to reflect well the experimental observations, 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 Supporting Information 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* ($5 \times 10^{10}\text{ s}^{-1}$, compared to $\approx 6 \times 10^{10}\text{ s}^{-1}$ in the trajectories) and the *A/B* ratio (10:1, versus 9:1 in the trajectories). On the other hand, for the *R*=tetramethylhexadecyl system, RRKM theory is off by three orders of magnitude in predicting the rate of cleavage *B* ($4 \times 10^7\text{ s}^{-1}$, compared to $\approx 4 \times 10^{10}\text{ s}^{-1}$ in the trajectories) along with being off by a factor of 31 in the *A/B* ratio (343:1, versus 11:1 in the trajectories).

The success of RRKM theory with 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 there is a significant time lag in the trajectories between the formation of the **PO** (median time 71 fs) and the rise of cleavage B events (>200 fs). This contrasts with the non-statistical 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 (more precisely a subset of the normal modes localized in that portion of the molecule), then an approximate statistical model may be developed to interpret our experimental observations. Following an extension of a process used previously by Rabinovich,^{10a} our model assumes that the ensemble of energies E^t within the molecular subset decays exponentially from the initial ensemble of energies E^0 , i. e. by eq 1, and it assumes 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 calculable from eq 2, where $PO^*(t)$ is the amount of energetic **PO** that survives to time t (decreased by $k_A(E^t)$ and $k_B(E^t)$). The decay constant λ is then set for each reaction to the value that affords the experimental product ratio.

$$E^t = E^0 e^{-\lambda t} \quad (1)$$

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

The λ 's obtained in this way are $1.6 \times 10^{11} \text{ s}^{-1}$, $2.5 \times 10^{11} \text{ s}^{-1}$, $3.5 \times 10^{11} \text{ s}^{-1}$, $4.2 \times 10^{11} \text{ s}^{-1}$, $4.9 \times 10^{11} \text{ s}^{-1}$, and $5.5 \times 10^{11} \text{ s}^{-1}$, 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 they appear quite consistent with directly-measured rate constants for IVR seen in time-resolved laser spectroscopic studies of alkyl-bridged azulene-anthracene systems by Schwarzer.¹⁶ These λ 's also fit well with the rates of energy loss to the alkyl groups seen above in the trajectories studies (a λ of $4 \times 10^{11} \text{ s}^{-1}$ corresponds to an energy loss of about 20 kcal/mol in 1 ps). The particular λ values depend on both the applicability of the model and the accuracy of the calculated barriers,¹⁷ so there is some danger of their overinterpretation, but it is interesting that the λ 's for the larger alkyl groups are over a factor of two greater than that for the methyl system. This suggests that most of the **PO** cooling in the larger systems is intramolecular as opposed to loss of energy to the solvent, as would be consistent with direct observations of vibrational relaxation by Crim.¹⁸

When an experimental product ratio does not fit with a theoretically calculated selectivity based on 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 will normally be perfectly correct, but the results here show that it need not be so, even for simple reactions in solution. The process applied here 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; the idea that large molecules might behave like smaller molecules for example was suggested by Rice in 1930.¹⁹ However, the results here 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.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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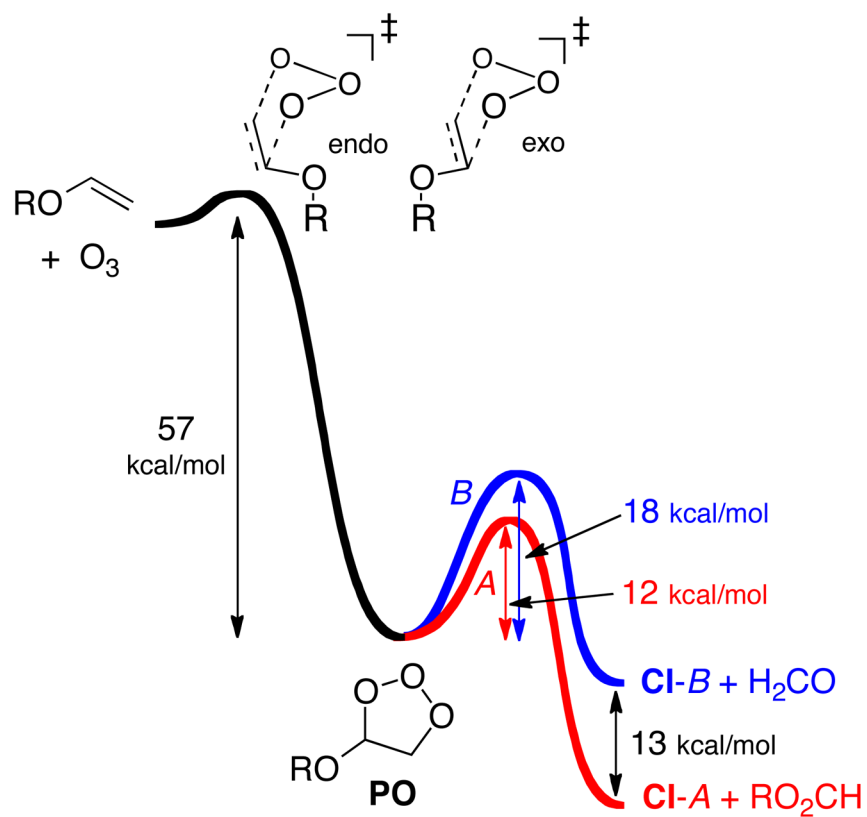


Figure 1. Free-energy profile for the reaction of ozone with vinyl ethers, based on G4 calculations. The particular energy values vary depending on the choice of alkyl group by <1 kcal/mol.

Table 1

Experimental and Statistically Predicted Product Ratios.

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

^aThe ratios given are based on the ¹H NMR integration for the methine peak of **3** versus the formyl peak of **1**.

^bUncertainties are 95% confidence ranges, with the number of measurements given in parentheses.

^cThe reactions were conducted at -55 °C unless otherwise noted.

^dGaussian-4 (G4) energetics were used for R=methyl, ethyl, and butyl. For the larger alkyl groups the R=butyl G4 relative energies were used, including a small correction factor for differences in the relative energies seen in B3LYP/6-311+G(2d,p) calculations.

^eThe two lowest-energy cleavage-A and two lowest-energy cleavage-B TSs were allowed for in all calculations.

^fThe TST calculations assume that the **PO** is thermally equilibrated while the RRKM calculations assume that there is no collisional energy transfer to the solvent.

Table 2Trajectory Results and Projected Cleavage *B* and *A/B* Ratios

alkyl group	<i>endo</i> TS	<i>exo</i> TS	projected <i>B</i> after 1 ps ^a	projected <i>A/B</i> ^b
methyl	A: 522 B: 38 (1.0%) no rxn: 3129	A: 1147 B: 129 (2.2%) no rxn: 4470	3.6%	27
ethyl	A: 420 B: 36 (0.6%) no rxn: 5423	A: 1089 B: 131 (2.3%) no rxn: 4445	2.8%	35
butyl	A: 395 B: 24 (0.4%) no rxn: 5731	A: 1075 B: 119 (2.1%) no rxn: 4564	2.2%	45
octyl	A: 417 B: 27 (0.4%) no rxn: 7136	A: 560 B: 52 (1.6%) no rxn: 2655	1.8	55
3,7-dimethyloctyl	A: 258 B: 24 (0.4%) no rxn: 5278	A: 811 B: 61 (1.3%) no rxn: 3872	1.7%	57
3,7,11,15-tetramethylhexadecyl	A: 265 B: 12 (0.3%) no rxn: 4163	A: 561 B: 51 (1.5%) no rxn: 2709	1.6%	62

^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 text).

^b Calculated as (100−%B)/%B.