Computational Study of the Thermochemistry of N_2O_5 and the Kinetics of the Reaction $\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2 \text{HNO}_3$

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Supporting Information

ABSTRACT: The multistructural method for torsional anharmonicity (MS-T) is employed to compute anharmonic conformationally averaged partition functions which then serve as the basis for the calculation of thermochemical parameters for N_2O_5 over the temperature range 0–3000 K, and thermal rate constants for the hydrolysis reaction $\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2 \text{HNO}_3$ over the temperature range 180–1800 K. The M06-2X hybrid meta-GGA density functional paired with the MG3S basis set is used to compute the properties of all stationary points and the energies, gradients, and Hessians of nonstationary points along the reaction path, with further energy refinement at stationary points obtained via single-point CCSD(T)-F12a/cc-pVTZ-F12 calculations including corrections for core–valence and scalar relativistic effects. The internal rotations in dinitrogen pentoxide are found to generate three structures (conformations) whose contributions are included in the partition function via the MS-T formalism, leading to a computed value for $S_{298.15}^\circ(\text{N}_2\text{O}_5)$ of $353.45 \text{ J mol}^{-1} \text{ K}^{-1}$.

This new estimate for $S_{298.15}^\circ(\text{N}_2\text{O}_5)$ is used to reanalyze the equilibrium constants for the reaction $\text{NO}_3 + \text{NO}_2 = \text{N}_2\text{O}_5$ measured by Osthoff et al. [*Phys. Chem. Chem. Phys.* **2007**, *9*, 5785–5793] to arrive at $\Delta_f H_{298.15}^\circ(\text{N}_2\text{O}_5) = 14.31 \pm 0.53 \text{ kJ mol}^{-1}$ via the third law method, which compares well with our computed *ab initio* value of $13.53 \pm 0.56 \text{ kJ mol}^{-1}$. Finally, multistructural canonical variational-transition-state theory with multidimensional tunneling (MS-CVT/MT) is used to study the kinetics for hydrolysis of N_2O_5 by a single water molecule, whose rate constant can be summarized by the Arrhenius expression $9.51 \times 10^{-17} (T/298 \text{ K})^{3.354} e^{(-7900 \text{ K}/T)} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 180–1800 K.

1. INTRODUCTION

A key oxidant in the nighttime troposphere is the nitrate radical (NO_3), whose concentration is dominated by the formation step

and the reversible process

NO_3 is largely consumed by reactions with volatile organic compounds, but the less reactive dinitrogen pentoxide (N_2O_5) is thought to be lost mainly via dry deposition and heterogeneous hydrolysis to nitric acid,¹ which represents an overall sink for nitrogen oxides in the troposphere and in the stratosphere. The homogeneous gas-phase step

is very slow, and a laboratory determination, by Wahner et al.,² yields a rate constant k_3 at 293 K of $2.5 \times 10^{-22} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This process would therefore be expected to be too slow to play a significant role in shifting atmospheric concentrations of nitrogen oxides. Aircraft measurements by Brown et al.³ in anthropogenic plumes of NO_x indeed indicate a major role for heterogeneous hydrolysis of N_2O_5 on aerosol particles. This work also showed that under some conditions where these

particles were sparse, the atmospheric lifetime of N_2O_5 was longer than anticipated based on gas-phase hydrolysis alone. Possibly k_3 has been overestimated. This observation is part of the motivation for the present study, where we evaluate the kinetics of R3 by computational methods.

The hydrolysis reaction has been the subject of several computational studies.^{4–8} These confirm that there is a significant reaction barrier and reveal that the presence of more than one water molecule in the transition state (TS) dramatically increases the reactivity. The most recent study by Voegelé et al.⁸ used G3B3 energies at B3LYP/6-31+G geometries and frequencies for points along the reaction coordinate for R3, and yielded $k_3 = 5.2 \times 10^{-25} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. This value is about five hundred times smaller than the experimental estimate, and if correct would suggest complications in the interpretation of the experiments. It includes a factor of ~ 1000 increase to allow for torsional motions in N_2O_5 and the transition state for R3. This seems a surprisingly large factor, and part of the present work is to consider the impact of deviations from the harmonic oscillator model in the reactants and TS for reaction R3.

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Figure 1. Reactant, product, and transition state structures for reaction R3 obtained using the M06-2X/MG3S electronic model chemistry. All energies are zero-point exclusive.

The N_2O_5 molecule is also of fundamental interest. As may be seen from the structure shown in Figure 1, the possibility of rotations of the NO_2 groups around the bonds to the central O atom make this an example of a relatively simple molecule that contains two internal rotors with high moments of inertia. They are likely to couple with each other and the overall rotation of the molecule. Interpretations of N_2O_5 electron diffraction data and microwave and FT-IR spectra yield a nonplanar C_2 geometry.^{9–12} The potential energy surface for the torsional motions is fairly flat, with shallow minima and modest barriers between conformations.¹² This means that simple models for internal rotors may be poor approximations. For example, Osthoff et al.¹³ considered several models for the internal rotors to assess various entropies in order to analyze their van't Hoff plot for the measured equilibrium constants for reaction R2. Different models correspond to different values for the low frequency modes, to which the entropy is most sensitive. The lowest two modes correspond to the symmetric and asymmetric combinations of the two torsions. A second aim of the present work is to eliminate this uncertainty in the entropy, and by reanalysis of the experiments with an accurate model of the two torsional modes to obtain a more firm value for the enthalpy of formation of N_2O_5 . We also derive this quantity via a directly computational approach, by the application of coupled cluster methods to the isodesmic reaction R3. Because the number and type of bonds are conserved, we are able to take advantage of error cancellation to obtain an accurate result. There have been prior computational studies of the thermochemistry of N_2O_5 , for instance those by

Janoschek and Kalcher¹⁴ who employed G3MP2B3 theory to obtain heats of formation of nitrogen oxides via atomization enthalpies, and by Jitariu and Hirst¹⁵ and Glendening and Halpern¹⁶ who used G2M and coupled cluster theory, respectively, to investigate the equilibrium R2. This required assessment of the difficult theoretical target NO_3 , where vibronic and electronic coupling and pseudo-Jahn–Teller distortion complicate the electronic and vibrational structure.¹⁷

The overall goals of the present work are to take advantage of recent advances in our understanding of anharmonic behavior within molecules and transition states to obtain improved estimates of the thermochemistry and kinetics of N_2O_5 relevant to atmospheric chemistry.

2. THEORETICAL APPROACH

2.1. Anharmonic Partition Functions. Accurate partition functions are central to the computation of reliable thermochemistry and thermal rate constants. The rigid-rotor, harmonic-oscillator (RRHO) model usually employed in the computation of partition functions for small molecules becomes an unphysical theoretical framework when applied to molecules or transition states in which vibrational motions such as torsions are possible, as these large-amplitude motions are highly anharmonic and can—quite drastically in some cases—affect the principal moments of inertia. In the absence of significant rotational–vibrational coupling, simple one-dimensional hindered rotor models can provide an adequate treatment of the torsional anharmonicity in a single-torsion species, provided that the torsional motion is also not strongly

coupled to other vibrations. However, due to their inherently limiting designs, the extension of such independent-torsion models to systems with multiple torsions is generally ill-advised because, in all but a few ideal cases, the coupling between torsions leads to stable conformations whose contributions to the partition function are entirely missed by such models. In fact, in cases where torsional coupling is significant, even the assignment of a particular normal mode to a specific torsion becomes highly problematic, which further invalidates the use of independent-torsion models for systems in which such effects can arise.

In this work, we utilize the multistructural method for torsions (MS-T)¹⁸ developed by Truhlar and co-workers to compute accurate partition functions that account for the effects of torsional anharmonicity in N₂O₅, HNO₃, and the transition states for reaction R3. The MS-T method captures the effects of torsional anharmonicity in species with multiple torsions by properly accounting for the contributions of all the structures that can be generated through the coupling of torsions and by reasonably approximating the multidimensional anharmonic potentials that connect these minima.¹⁸ Unlike independent torsion models, provisions are made in the MS-T treatment to account for the coupling between torsions to each other and to the overall rotation via the Kilpatrick–Pitzer scheme.¹⁹ Collectively, these features enable the MS-T method to model the dynamical nature of flexible multitorsion species more physically.

The MS-T method (also called MS-T(U) in a recent publication²⁰) has been described in detail elsewhere,¹⁸ so we only briefly highlight its main features here. The MS-T procedure relies on the number of conformers and their geometries, frequencies, and relative energies to evaluate the partition functions at the low temperature limit—the local-harmonic oscillator regime—and at the high temperature limit—the free-internal-rotor regime. These two limiting cases serve as end-points between which anharmonic partition functions in the hindered internal rotor (intermediate temperature) regime are obtained via an interpolation ansatz^{18,21} that provides a physical description of the expected temperature dependence of the partition functions within the approximations of the overall model. The problem of associating normal modes with specific torsions is circumvented in the MS-T treatment through the use of both Cartesian normal coordinates and curvilinear internal coordinates at different stages of the calculation. After all of the torsional conformers of a species have been characterized, the MS-T conformational rotational–vibrational partition functions are calculated via

$$Q_{\text{con-rovib}}^{\text{MS-T}} = \sum_{j=1}^J Q_j^{\text{rot}} \exp\left(-\frac{U_j}{k_B T}\right) Q_j^{\text{HO}} Z_j \prod_{\tau=1}^t f_{j,\tau} \quad (1)$$

where Q_j^{rot} is the classical rotational partition function of structure j , k_B is Boltzmann's constant, and Q_j^{HO} is the typical normal-mode harmonic oscillator vibrational partition function calculated at structure j , which leads to a conformationally averaged partition function upon summation over all the structures. The Z_j factor ensures that the correct partition functions (within the framework of the MS-T model) are reached at the high-temperature limit, and the combination of the Z_j factor with the torsional anharmonicity function $f_{j,\tau}$ correct the partition function of structure j for the effects of the anharmonic potentials of each of its torsions, τ . The distinguishable structures of a reactant, product, or transition

state are labeled by $j = 1, 2, \dots, J$ (where J is the total number of respective reactant, product, or TS structures) in the above expression. Therefore, for each species, U_j denotes the potential energy of structure j with respect to the lowest-potential-energy structure for that particular species, which is always labeled with the index $j = 1$ by convention; thus, U_1 is zero by definition. Note that these partition functions are calculated relative to the energy of the global minimum on the potential energy surface, i.e., not relative to the zero-point energy.

For practical purposes, it is often informative to track how the ratio of the MS-T partition function to that of the usual RRHO partition function computed from a single structure (which we denote as SS-RRHO in this article) changes as a function of temperature. Within the context of MS-T, this ratio is usually referred to as the “ F -factor,”^{22,23} which is given by

$$F_{\alpha}^{\text{MS-T}} = \frac{Q_{\text{con-rovib},\alpha}^{\text{MS-T}}(T)}{Q_{\alpha}^{\text{SS-RRHO}}(T)} \quad (2)$$

for any given species α at a specific temperature. These F -factors can be broken down further into a multistructural, local-harmonic component and a torsional component, $F_{\alpha}^{\text{MS-LH}}$ and F_{α}^{T} , respectively, which provide approximate measures of the extents to which the overall partition function is affected by conformationally averaging over all torsional conformers of a species (as opposed to computing the partition function from a single structure), and how much it is affected by accounting for the anharmonic features of the potential energy along torsional coordinates:

$$F_{\alpha}^{\text{MS-T}} = F_{\alpha}^{\text{MS-LH}}(T) F_{\alpha}^{\text{T}}(T) = \left(\frac{Q_{\text{con-rovib},\alpha}^{\text{MS-LH}}(T)}{Q_{\alpha}^{\text{SS-RRHO}}(T)} \right) \times \left(\frac{Q_{\text{con-rovib},\alpha}^{\text{MS-T}}(T)}{Q_{\text{con-rovib},\alpha}^{\text{MS-LH}}(T)} \right) \quad (3)$$

In the above equation, $Q_{\text{con-rovib},\alpha}^{\text{MS-LH}}$ is the multistructural local-harmonic partition function and is obtained by setting all of the $f_{j,\tau}$ and Z_j equal to unity in eq 1, i.e., the contributions from all structures are included but the torsional potential in the vicinity of each local minimum is approximated as a harmonic oscillator with infinitely high barriers separating it from other minima (structures).

2.2. Thermochemistry. One aim of the present article is to derive accurate estimates for the thermochemistry of N₂O₅. We take two approaches here. The first is to calculate the overall enthalpy change for reaction R3 ($\Delta H^{\circ}_{\text{R3}}$) and then combine it with the experimental enthalpies of formation for H₂O and HNO₃ to arrive at the heat of formation of N₂O₅. This method relies on the *ab initio* energetics. The second approach relies instead on the *ab initio* entropy, where we combine the thermodynamic quantities C_p° , S° and $H_T - H_{298.15}$ for N₂O₅ with data for NO₃ and NO₂ to reanalyze the equilibrium measurements of reaction R2 by Osthoff et al.¹³ and obtain an experimentally based heat of formation of N₂O₅.

We use the *MSTor* program²⁴ to evaluate the enthalpy H° and entropy S° over the temperature range 0–3000 K at a standard state pressure of 1 bar. The *MSTor* program computes the anharmonic partition functions using the MS-T method, and then calculates the thermochemical parameters of interest via standard relations²⁵ from statistical mechanics:

$$H^\circ(T) = k_B T^2 \frac{\partial [\ln(Q_{\text{con-rovib},\alpha}^{\text{MS-T}}(T))]}{\partial T} + P^\circ V \quad (4)$$

$$S^\circ(T) = k_B \ln(Q_{\text{con-rovib},\alpha}^{\text{MS-T}}(T)) + k_B T \left(\frac{\partial \ln(Q_{\text{con-rovib},\alpha}^{\text{MS-T}}(T))}{\partial T} \right) \quad (5)$$

We also report the constant pressure heat capacity, C_p° , which was evaluated via the *MSTor* program using a four-point central finite differences method with a step size (δT) of 1 K:

$$C_p^\circ(T) = \left(\frac{\partial H}{\partial T} \right)_p \approx [H^\circ(T - 2\delta T) - 8H^\circ(T - \delta T) + 8H^\circ(T + \delta T) - H^\circ(T + 2\delta T)]/12\delta T \quad (6)$$

The computed thermochemistry is also impacted by the accuracy of the vibrational zero-point energies (ZPEs) for the reactants and products of R3. Most often, ZPEs are approximated by scaling the harmonic frequencies by an appropriate scale factor and then taking the half sum of these scaled frequencies. The recommended scale factor for estimating the ZPE of a stable molecule from the harmonic frequencies computed with M06-2X/MG3S is 0.970.²⁶ However, this scale factor was optimized based on the properties of small rigid molecules and may not be optimal for some of the larger, more flexible (i.e., torsion-containing) species of present interest. Therefore, we use hybrid degeneracy-corrected second-order vibrational perturbation theory²⁷ to compute anharmonic ZPEs and establish individual scale factors for N_2O_5 , HNO_3 , and the TS for R3. To establish the scale factor for H_2O , we use the literature²⁸ value of $55.46 \pm 0.25 \text{ kJ mol}^{-1}$ for the experimental ZPE of this species.

2.3. Thermal Rate Constants. The thermal rate constants for reaction R3 are calculated using multistructural canonical variational transition state theory with multidimensional tunneling (MS-CVT/MT).²² By substituting the MS-T partition functions for the SS-RRHO partition functions normally used in CVT calculations, MS-CVT extends the applicability of CVT to the kinetics of complex reactions involving reactants and/or transition states with multiple structures generated through torsions (some or all of which may be strongly coupled). As shown in eq 7, the transformation of CVT/MT into MS-CVT/MT is conveniently accomplished by multiplying the usual single-structure CVT/MT rate constant by a reaction-specific factor $F^{\text{MS-T}}$

$$k^{\text{MS-CVT/MT}} = F^{\text{MS-T}}(T) k^{\text{CVT/MT}}(T) \quad (7)$$

where the reaction-specific factor $F^{\text{MS-T}}$ is simply the ratio of species-specific F -factors for the conventional TS and the reactant(s) introduced in section 2.1:

$$F^{\text{MS-T}} = \frac{F_{\text{TS}}^{\text{MS-T}}(T)}{\prod_{i=1}^N F_{\text{R},i}^{\text{MS-T}}(T)} \quad (8)$$

The effects of quantum mechanical tunneling on the MS-CVT rate constant for reaction R3 are calculated using a semiclassical model based on the small-curvature (multidimensional) tunneling (SCT) approximation.^{29,30} Within the context of the SCT approximation, one computes the ground-state transmission coefficient κ^{SCT} as the ratio between the averaged semiclassical (vibrationally) adiabatic ground-state transmission

probability and the averaged ground-state quasiclassical transmission probability.^{31,32} The effects of tunneling are then incorporated into the final rate constant by multiplying the quasiclassical MS-CVT rate constant (i.e., the rate constant evaluated by accounting for quantum mechanical effects in vibrational modes transverse to the reaction coordinate but with motion along the reaction coordinate itself assumed to be classical) by the ground-state transmission coefficient κ^{SCT} .^{31,32} The effect of nonclassical reflection on the rate constant is also included in κ^{SCT} . An underlying assumption in the SCT model is that the ground-state vibrationally adiabatic potential curve, V_a^G , is a fairly reasonable representation of the shapes of the excited-state vibrationally adiabatic potential curves,^{33,34} consequently, all of the tunneling probabilities are evaluated using the V_a^G as the sole effective potential in the SCT approximation. The V_a^G potential curve is constructed by adding the local zero-point vibrational energy of the bound modes transverse to the reaction coordinate s , denoted as ϵ^G , to the potential energy along the minimum energy path $V_{\text{MEP}}(s)$:

$$V_a^G = V_{\text{MEP}}(s) + \epsilon^G(s) \quad (9)$$

Since ϵ^G depends on s , any transmission coefficient based on ϵ^G is nominally multidimensional as it already includes one effect of the nonseparability of the reaction coordinate. In addition, the SCT method is designed also to capture the effects of corner-cutting^{35–37} tunneling for reaction systems in which the minimum energy path (in isoinertial coordinates) exhibits small curvature. This curvature is due to the coupling between the reaction coordinate and the modes transverse to it, giving rise to a negative centrifugal effect that shortens the tunneling path. Consequently, neglecting to account for the multidimensional nature of the tunneling path brought about by the coupling between the reaction coordinate and the transverse modes can lead to appreciable underestimation of the tunneling contribution, which is circumvented in the SCT method by using an effective mass that accounts for the centrifugal effect in the calculation of the tunneling probabilities,^{29,30} as opposed to setting the effective mass equal to the constant reduced mass by which the isoinertial coordinates are scaled. Tunneling models beyond the SCT approximation can add considerable computational expense but may also improve the accuracy of the estimated tunneling contribution for reaction systems in which the MEP exhibits large curvature, in which case the adiabatic approximation often breaks down. However, the MEP for R3 is relatively broad, so one would expect the contributions due to small-curvature tunneling to dominate at the temperatures of interest in the present article, which was in fact demonstrated by Voegele et al.⁸ for the present reaction system, validating the use of the SCT model as a reasonable approximation to the tunneling in R3.

2.4. Computational Details. The stationary points along the potential energy surface for reaction R3 were characterized using the M06-2X³⁸ hybrid meta-GGA density functional and the MG3S³⁹ minimally augmented basis set—a high-performance combination which has been shown to give reliable geometries and frequencies for reaction systems of comparable size to R3.^{40–42} To ensure numerical convergence, all M06-2X/MG3S calculations employed a large integration grid consisting of 99 radial shells around each atom and 974 angular points in each shell (99 974). Because of the presence of coupled torsions in this reaction system, comprehensive structure searches were carried out along the torsional coordinates in

N_2O_5 and the TS for R3 (as well as around the single torsion in HNO_3), also using M06-2X/MG3S, and the optimized geometries and Hessians for all torsional conformers located for each of these species were then used to obtain their respective MS-T partition functions. All internal degrees of freedom were scaled by species-specific empirical scale factors determined in this work, which will be discussed in the next section. The classical energies of the lowest-energy conformers (at the M06-2X/MG3S level of theory) of all species along the reaction coordinate were further refined via high-level single-point CCSD(T)-F12a/cc-pVTZ-F12^{43–45} calculations. These calculations are meant to approximate the CCSD(T) result in the complete basis set (CBS) limit efficiently, which was verified using the two-point CBS extrapolation scheme proposed by Halkier et al.,⁴⁶ for which we used the cc-pVnZ triple- ζ and quadruple- ζ correlation consistent basis sets with no augmentation. Finally, the CCSD(T)-F12a/cc-pVTZ-F12//M06-2X/MG3S energies are corrected for core–valence (CV) and scalar relativistic (R) effects using the same methodology as developed for the W1 method by Martin and co-workers,⁴⁷ namely, by evaluation of the difference between the energy from the CCSD(T)/MTsmall level of theory with the core electrons excluded from correlation, and the energy from a Douglas–Kroll–Hess second-order CCSD(T) calculation with the same basis set and with all electrons correlated. The ensuing CCSD(T)-F12a/cc-pVTZ-F12//M06-2X/MG3S + CV + R barrier height and energy of reaction, and the M06-2X/MG3S partition functions for dinitrogen pentoxide, water, and the TS were then used as input parameters in the calculation of thermal rate constants for the R3 via MS-CVT/SCT.

The POLYRATE program⁴⁸ was used to compute the CVT rate constants and SCT tunneling correction for R3 via direct dynamics. In this work, the direct dynamics approach entailed constructing the V_{MEP} and V_a^G profiles “on the fly” from the energies, gradients, and force constants of points along the MEP for R3 computed using the M06-2X/MG3S electronic model chemistry. The MPM algorithm⁴⁹ (a modification of the original Page-McIver algorithm⁵⁰ that allows for the Hessians to be used at non-Hessian steps) was used to calculate the MEP using a step size of 0.005 Å—in isoinertial coordinates scaled to a reduced mass of 1 amu—and updating the Hessian every ninth step. The frequencies for the vibrations transverse to the reaction path needed for the calculation of the V_a^G were scaled by 0.979, a value that will be discussed in the next section. The CCSD(T)-F12a/cc-pVTZ-F12 single-point calculations were carried out using the MOLPRO program.⁵¹ The Gaussian 09 program suite⁵² was used to perform all other electronic structure calculations reported in this article, including the calculations required for the direct dynamics analysis in POLYRATE. The GAUSSRATE program⁵³ is used to interface POLYRATE with the Gaussian 09 program suite.

3. RESULTS AND DISCUSSION

3.1. Zero-Point Energies and Scale Factors. In general, scale factors for ZPEs are used to compensate approximately for two different deficiencies: the intrinsic error of the electronic structure method with regard to calculating the “true” harmonic frequencies—which is method-specific—and a correction for the anharmonicity of the ZPE—which is structure-specific. The scale factor for ZPEs can thus be viewed as the product of the scale factor for correcting for the inexactness of the electronic structure theory in question (M06-2X/MG3S in the present case) in computing the “true”

harmonic frequencies and the scale factor for anharmonicity. The former of these is known to be 0.982 for M06-2X/MG3S.²⁶ To obtain the scale factor for the latter effect, we follow the prescription of Zheng et al.,⁵⁴ whereby we compute the anharmonic ZPE for the species of interest using hybrid degeneracy-corrected second-order vibrational perturbation theory²⁷ and take the ratio of this ZPE to the harmonic ZPE (i.e., the half sum of the computed harmonic frequencies).

The harmonic ZPEs computed with M06-2X/MG3S (based on the frequencies provided in the Supporting Information) for the reactants, products, and TS of R3 are given in Table 1. The

Table 1. ZPEs in kJ mol^{-1} and ZPE Scale Factors (λ^{ZPE}) for N_2O_5 , HNO_3 , and H_2O and the TS for R3a

property	N_2O_5	HNO_3	H_2O	TS _{R3a}
harmonic ZPE	75.45	72.05	56.87	139.50
anharmonic ZPE	74.90	71.43	—	139.14
ZPE ^a best estimate	73.55	70.15	55.46	136.64
λ^{ZPE}	0.975	0.974	0.975	0.979

^aDerived by scaling the Anharmonic ZPE by 0.982 for N_2O_5 , HNO_3 , and the TS. For H_2O , this value comes from Irikura et al.²⁸

anharmonic ZPEs computed via hybrid degeneracy-corrected second-order vibrational perturbation theory²⁷ are also provided in Table 1, as are the ensuing species-specific ZPE scale factors. It is interesting to note that the scale factors for the stable species were all encompassed within the narrow range of 0.974–0.975, which is close to the recommended scale factor value of 0.970.²⁶ Finally, the scale factor for the ZPE of the TS was derived to be 0.979. A possible rationalization of the marginally larger scale factor for the TS is perhaps that the ring makes the TS more rigid than N_2O_5 . These newly derived scale factors for the reactants, products, and transition state of R3 will be subsequently used in the MSTor and POLYRATE calculations.

The literature value for the ZPE of H_2O , 55.46 kJ mol^{-1} —which is exactly duplicated by scaling the harmonic ZPE computed via M06-2X/MG3S by the scale factor in Table 1—has an associated 2σ uncertainty of $\pm 0.25 \text{ kJ mol}^{-1}$.²⁸ Using our estimates of the ZPEs for H_2O , N_2O_5 , and HNO_3 , we obtain a ZPE difference between the products and reactants of R3 of 11.28 kJ mol^{-1} , and to place a lower bound on the uncertainty in this quantity, we assume that the 2σ uncertainty in our estimated ZPEs is no less than that reported for the literature ZPE value of H_2O , yielding a 2σ uncertainty for the ZPE difference in R3 of at least $\pm 0.50 \text{ kJ mol}^{-1}$.

3.2. Partition Functions and Thermochemistry. The ratio of the MS-T partition function to the SS-RRHO partition function for N_2O_5 , $F_{\text{N}_2\text{O}_5}^{\text{MS-T}}$, its multistructural, local-harmonic component, $F_{\text{N}_2\text{O}_5}^{\text{MS-LH}}$, and its torsional component, $F_{\text{N}_2\text{O}_5}^{\text{T}}$, are given in Table 2. Three torsional conformers were located for N_2O_5 and, as depicted in Figure 1, two of these are nonsuperposable mirror image structures within the C_2 point group, while the third is a C_s structure 0.28 kJ mol^{-1} higher in energy (0.25 kJ mol^{-1} higher after the inclusion of scaled ZPEs) than the degenerate C_2 structures. The identification of the lowest-energy conformation of N_2O_5 as C_2 , not C_s , is consistent with experimental observations. Because HNO_3 has only one torsional conformation (i.e., the two minima along its torsional potential are superposable mirror images), $F_{\text{HNO}_3}^{\text{MS-T}}$ for this species is equivalent to just its torsional component $F_{\text{HNO}_3}^{\text{T}}$.

Table 2. Species-Specific and Reaction-Specific Multi-Structural Factors for Equation 3

T (K)	$F_{\text{N}_2\text{O}_5}^T$	$F_{\text{N}_2\text{O}_5}^{\text{MS-LH}}$	$F_{\text{N}_2\text{O}_5}^{\text{MS-T}}$	$F_{\text{TS}}^{\text{MS-LH}}$	$F_{\text{HNO}_3}^T$	$F_{\text{R3}}^{\text{MS-T}}$
180	1.17	5.58	6.53	2.05	1.01	0.31
200	1.19	5.66	6.71	2.08	1.01	0.31
250	1.22	5.82	7.08	2.18	1.02	0.31
298.15	1.24	5.92	7.33	2.30	1.02	0.31
300	1.24	5.92	7.34	2.31	1.02	0.31
400	1.26	6.06	7.62	2.61	1.03	0.34
600	1.23	6.19	7.63	3.23	1.05	0.42
800	1.16	6.25	7.27	3.76	1.07	0.52
1000	1.08	6.29	6.78	4.17	1.10	0.62
1200	0.99	6.32	6.28	4.51	1.12	0.72
1500	0.88	6.34	5.57	4.91	1.14	0.88
1800	0.78	6.36	4.96	5.20	1.16	1.05

which is also provided in Table 2. As can be seen from Table 2, the temperature dependence of the torsional component for each of these molecules captures the expected physical behavior for torsions. At low temperature the contributions of these anharmonic motions to the partition function are well-described by the harmonic oscillator model, but as the temperature continues to increase, clear discrepancies begin to arise between the two models, whereby the harmonic oscillator model first underestimates the partition function in the hindered internal rotation regime, and then increasingly overestimates the partition function—while the anharmonic partition function falls off toward its free rotor limit, the harmonic partition function continues to increase and eventually becomes unphysical, extending past the $0-2\pi$ torsional space.

Table 2 also shows that the contribution to the MS-T partition function for N_2O_5 due to conformationally averaging over all three of its structures, $F_{\text{N}_2\text{O}_5}^{\text{MS-LH}}$, is much more significant than the contribution made by $F_{\text{N}_2\text{O}_5}^T$ at all temperatures considered. In the limit of low temperature, the MS-LH factor approaches the value of the degeneracy for the ground state, which is 2 because of the two nonsuperposable mirror image C_2 structures in the case of N_2O_5 , and this value would remain constant with increasing temperature if no other conformations were included in the calculation of the MS-T partition function. However, because the third structure for N_2O_5 is relatively close in energy to the lowest-energy conformer(s), the contribution of this structure is appreciable even at low temperatures, for example, at 50 K this structure already comprises about 50% of the total value for $F_{\text{N}_2\text{O}_5}^{\text{MS-LH}}$. In principle, if the SS-RRHO partition function of structure 3 were equal to that of the lowest-energy structure, $F_{\text{N}_2\text{O}_5}^{\text{MS-LH}}$ would monotonically converge to a value of 3 in the limit of high temperature, with each structure making an equal contribution; however, a glance at Table 2 reveals that this is not the case, with structure 3 contributing 336% more than that by 1800 K, resulting from the fact that the product of its moments of inertia and its vibrational spacing are both smaller than those for the lowest-energy structure(s).

The thermodynamic quantities C_p° , S° and $H_T - H_{298.15}$ for N_2O_5 over the temperature range 0–3000 K and at the standard pressure of 1 bar—calculated from its MS-T partition function—are summarized in Table 3. The reaction enthalpy for R3 at 0 K, ΔH_0° , was computed to be -35.06 ± 0.50 kJ mol $^{-1}$ using the CCSD(T)-F12a/cc-pVTZ-F12//M06-2X/

Table 3. Thermodynamic Data for N_2O_5 (Standard State Pressure = 0.1 MPa)

T (K)	C_p° (J K $^{-1}$ mol $^{-1}$)	S° (J K $^{-1}$ mol $^{-1}$)	$H^\circ - H_{298.15}^\circ$ (kJ mol $^{-1}$)
0	0.00	0.00	−18.82
50	49.16	243.39	−16.60
100	55.55	279.46	−13.98
150	62.32	303.21	−11.05
200	70.51	322.24	−7.73
250	78.97	338.89	−3.99
298.15	86.52	353.45	0.00
300	86.79	353.99	0.16
350	93.70	367.90	4.67
400	99.74	380.81	9.51
450	105.01	392.87	14.64
500	109.60	404.17	20.00
600	117.11	424.84	31.35
700	122.87	443.35	43.37
800	127.29	460.04	55.89
900	130.73	475.24	68.79
1000	133.42	489.14	82.01
1100	135.56	501.95	95.46
1200	137.27	513.82	109.11
1300	138.65	524.85	122.90
1400	139.79	535.15	136.83
1500	140.73	544.82	150.85
1600	141.52	553.92	164.97
1700	142.18	562.51	179.15
1800	142.74	570.64	193.40
1900	143.22	578.35	207.70
2000	143.63	585.70	222.04
2100	143.99	592.71	236.43
2200	144.31	599.40	250.84
2300	144.58	605.81	265.28
2400	144.82	611.96	279.75
2500	145.04	617.86	294.25
2600	145.24	623.54	308.76
2700	145.41	629.01	323.29
2800	145.56	634.29	337.84
2900	145.70	639.39	352.41
3000	145.82	644.32	366.98

MG3S + CV + R data. This uncertainty comes solely from the estimated uncertainty in the ZPE difference for R3, as explained in section 3.1, and serves as a lower bound to the actual uncertainty in the calculated result. The combination of this computed ΔH_0° with the experimental heats of formation for H_2O and HNO_3 of -238.919 ± 0.027 and -124.45 ± 0.18 kJ mol $^{-1}$, respectively,⁵⁵ yields a value of 25.08 ± 0.56 kJ mol $^{-1}$ for the enthalpy of formation of N_2O_5 at 0 K, or $\Delta_f H_0^\circ(\text{N}_2\text{O}_5)$. This value is in agreement with the experimental value of 24.33 ± 0.35 kJ mol $^{-1}$ derived in the Active Thermochemical Tables (ATcT).⁵⁵ Using the $H_T - H_{298.15}$ literature values for O_2 and N_2 (8.683 and 8.670 kJ mol $^{-1}$, respectively)⁵⁶ and the computed $H_T - H_{298.15}$ for N_2O_5 (Table 2), we derive a value for the enthalpy of formation of N_2O_5 at 298.15 K ($\Delta_f H_{298.15}^\circ$) of 13.53 ± 0.56 kJ mol $^{-1}$.

The recent measurements of the equilibrium constant for R2 by Osthoff et al.¹³ provide an alternate route to a value for $\Delta_f H_{298.15}^\circ(\text{N}_2\text{O}_5)$, via a third law analysis. The third law method requires knowledge of the entropy of reaction, which can then be used to fix the intercept in a constrained van't Hoff plot. In addition, knowledge of the integrated heat capacity for R2 also

permits the calculation of temperature correction terms⁵⁷ that can be applied to the $\ln K_p$ values to yield $\Delta H_{298.15}^\circ$ and $\Delta S_{298.15}^\circ$ for R2 directly from the slope and intercept of the van't Hoff plot. The heat capacity data used to calculate these corrections are given in Table S4 of Supporting Information.

The entropy and heat capacity values for N_2O_5 necessary for the third law analysis were taken from Table 3. For NO_2 , we use the $S_{298.15}^\circ$ value of $240.17 \text{ J mol}^{-1} \text{ K}^{-1}$ from Gurvich et al.⁵⁸ while the values for C_p° as a function of temperature were obtained by fitting the values tabulated at JANAF⁵⁶ for this quantity over the T range 100–500 K to the fourth order polynomial given in eq 10 (RMSD = $0.003 \text{ J mol}^{-1} \text{ K}^{-1}$). For NO_3 , we use the vibrational levels from the study by Stanton,¹⁷ in which the vibronic coupling in this pseudo-Jahn–Teller system was carefully accounted for, to derive the vibrational contribution to the partition function for this species via direct summation, and from this obtain the vibrational contribution to the thermodynamic functions of interest via standard relations.²⁵ The contributions to $S_{298.15}^\circ$ and $C_p^\circ(T)$ from translations and rotations were derived using the mass and the moments of inertia of NO_3 listed at the CCCBDB⁵⁹ (and a rotational symmetry number of 6), respectively, and an additional $\ln 2$ contribution was added to $S_{298.15}^\circ$ to account for the electronic degeneracy of the ground state. This yielded $S_{298.15}^\circ(NO_3) = 256.99 \text{ J mol}^{-1} \text{ K}^{-1}$. The values for the constant pressure heat capacities of NO_2 , NO_3 , and N_2O_5 at the temperatures at which Osthoff et al. reported measurements for K_p are also tabulated in Supporting Information (Table S4). The $\Delta_r C_p^\circ$ data for R2 were then fit to the fourth order polynomial in eq 11 (RMSD = $0.0005 \text{ J mol}^{-1} \text{ K}^{-1}$), which was then used to evaluate the integrated heat capacity for R2 and derive the small aforementioned corrections to K_p denoted as δ in Table S5 of the Supporting Information.

$$C_p^\circ = 35.1 - 3.94 \times 10^{-2}T + 2.40 \times 10^{-4}T^2 - 3.45 \times 10^{-7}T^3 + 1.73 \times 10^{-10}T^4 \quad (10)$$

$$\Delta_r C_p^\circ = -562 + 7.13T - 3.45 \times 10^{-2}T^2 + 7.49 \times 10^{-5}T^3 - 6.13 \times 10^{-8}T^4 \quad (11)$$

Using the set of entropies described above, we obtain a value of $\Delta S_{298.15}^\circ = -143.70 \text{ J mol}^{-1} \text{ K}^{-1}$ for R2, and the ensuing constrained van't Hoff plot for R2 is depicted in Figure 2. As can be seen from this figure, the fit passes through all of the data points. From the slope of the van't Hoff plot, we arrive at a value of $-93.80 \pm 0.49 \text{ kJ mol}^{-1}$ for the $\Delta H_{298.15}^\circ$ of R2, where the uncertainty was estimated from the deviation that could be introduced in the slope if the fit instead passed through ends of the upper or lower error bars for the data point at 278.1 K. This value is in agreement with the NASA-JPL recommendation⁶⁰ of $-94.6 \pm 3.4 \text{ kJ mol}^{-1}$, and also with the value of $-93.35 \pm 0.40 \text{ kJ mol}^{-1}$ obtained from ATcT.⁵⁵ Finally, we use the experimentally based enthalpies of formation at 298.15 K for NO_2 and NO_3 from ATcT (34.017 ± 0.064 and $74.09 \pm 0.19 \text{ kJ mol}^{-1}$, respectively) to arrive at the value of $\Delta_f H_{298.15}^\circ(N_2O_5) = 14.31 \pm 0.53 \text{ kJ mol}^{-1}$. This value is in agreement with our computed value of $13.53 \pm 0.56 \text{ kJ mol}^{-1}$, obtained from combining our computed thermochemistry for N_2O_5 with the literature⁵⁶ values for the thermochemistry of N_2 and O_2 .

The NASA-JPL group⁶⁰ recommended an expression for K_p based on different forward and reverse studies of the kinetics of R2, whose overlapping temperature range is 253–318 K.^{61,62}

Figure 2. Constrained van't Hoff plot (third law method) for R2. The open squares represent equilibrium constants from Osthoff et al. (ref 13) while the filled circles correspond to equilibrium constants recommended by NASA-JPL (ref 60). The solid line is the third law fit to the Osthoff et al. data and the dashed line is the fit to the equilibrium data recommended by NASA-JPL. Both sets of equilibrium constants include a small correction (calculated in this study) for the temperature dependence of ΔH and ΔS . The inset is an enlargement of the nonintercept data points in the temperature range 274–328 K and the third law fits to them, along with 2σ error bars in each case.

We evaluated K_p from the expression at five temperatures spanning this range and plot these data on Figure 2 as well. The agreement with the later Osthoff et al.¹³ results is very good. We repeated the same kind of van't Hoff analysis as detailed above (see Table S5), to obtain a reaction enthalpy value of $-93.35 \pm 0.58 \text{ kJ mol}^{-1}$ for R2 at 298.15 K, which results in a heat of formation for N_2O_5 at 298.15 K of $14.75 \pm 0.61 \text{ kJ mol}^{-1}$, in accord with the values derived above.

Table 4 summarizes the experimental thermochemistry for N_2O_5 available in the literature. All of these literature values seem to rely on the indirect determination of the entropy for N_2O_5 at 298 K from the kinetics experiments of Ray and Ogg.⁶³ In particular, both JANAF⁵⁶ and Gurvich et al.⁵⁸ use this entropy value to estimate the barriers to internal rotations in the simple one-dimensional hindered rotor models they each subsequently employed, which, according to Gurvich et al.,⁵⁸ led to the derivation of conflicting thermochemistry because the entropy value of Ray and Ogg was actually misinterpreted in the JANAF reference book. The $S_{298.15}^\circ$ computed in this study using MS-T partition functions, $353.45 \text{ J mol}^{-1} \text{ K}^{-1}$, is in very good agreement with the value from Ray and Ogg,⁶³ supporting the recommendations of Gurvich et al.⁵⁸ and NASA-JPL⁶⁰ over that listed at JANAF,⁵⁶ which is nearly $7 \text{ J mol}^{-1} \text{ K}^{-1}$ lower than the value we computed. The value for $\Delta_f H_{298.15}^\circ(N_2O_5)$ obtained from our third law analysis is also in agreement with the Gurvich et al.⁵⁸ and NASA-JPL⁶⁰ recommendations, and with the value listed at ATcT;⁵⁵ however, it is about 3 kJ mol^{-1} higher than that from JANAF.⁵⁶ The independent-torsion models used by the JANAF reference book and Gurvich et al. seem to have led to heat capacity values for N_2O_5 at room temperature that are in relatively good agreement with each other,^{56,58} but our more extensive treatment of torsions in the present work indicates that perhaps these estimates are about $9\text{--}10 \text{ J mol}^{-1} \text{ K}^{-1}$ too

Table 4. Summary of Available Thermochemical Parameters for N_2O_5

$\Delta_f H_0^\circ$ (kJ mol ⁻¹)	$\Delta_f H_{298.15}^\circ$ (kJ mol ⁻¹)	$C_{p,298.15}^\circ$ (J K ⁻¹ mol ⁻¹)	$S_{298.15}^\circ$ (J K ⁻¹ mol ⁻¹)	$H^\circ - H_{298.15}^\circ$ (kJ mol ⁻¹)	reference
			355.7 ± 2.1		Ray and Ogg ⁶³
	11.30	96.30	346.55		NIST-JANAF ⁵⁶
22.87	13.3 ± 1.5	95.33	355.7 ± 7	20.80	Gurvich et al. ⁵⁸
	13.3 ± 1.5		355.7 ± 7		NASA-JPL ⁶⁰
24.33 ± 0.35	14.76 ± 0.35				ATcT ⁵⁵
25.08 ± 0.56	13.53 ± 0.56	86.52	353.45	18.82	this work (ab initio)
	14.31 ± 0.53				this work (3rd law)

Table 5. Energetics for R3 in Units of kJ mol⁻¹ Obtained at Various Levels of Theory, All Based on M06-2X/MG3S Geometries

parameter	M06-2X/MG3S	CCSD(T)-F12a/cc-pVTZ-F12	CCSD(T)/2-point-CBS-extrap.	CV + R	CCSD(T)/CBS + CV + R ^b
ΔE	-61.65	-46.42	-45.99	0.08	-46.35
ΔH_0° ^a	-50.36	-35.14	-34.71	0.08	-35.06
$V_f^\ddagger$	60.68	68.32	68.05	-0.16	68.16
$\Delta_f V_a^{\ddagger \ddagger}$ ^a	68.31	75.95	75.68	-0.16	75.79

^aInclude the best estimates to the ZPEs from Table 1. ^bApproximated via CCSD(T)-F12a/cc-pVTZ-F12//M06-2X/MG3S + CV + R.

high. The only estimate of $H_T - H_{298.15}$ in the literature is from Gurvich et al.,⁵⁸ which is within 2 kJ mol⁻¹ of the value we obtain here via MS-T (Table 4).

3.3. Potential Energy Surface for Hydrolysis. Reaction R3 was found to proceed via two separate reaction channels, as also noted by Voegele et al.,⁸ one in which H_2O attacks one of the terminal oxygen atoms in N_2O_5 (which we label R3a) and one in which H_2O attacks the central oxygen atom in N_2O_5 (which we label R3b). Structure searches using the M06-2X/MG3S electronic model chemistry revealed that the TS for R3a has four structures that can be subgrouped into two sets of nonsuperposable mirror image pairs (which will be discussed in greater length in section 3.4), while the TS for R3b only has two structures, and these structures are nonsuperposable mirror images (Figure 1). Subsequent CCSD(T)-F12a/cc-pVTZ-F12//M06-2X/MG3S calculations showed that the lowest-energy conformation of the TS for R3a is lower in energy by 37.36 kJ mol⁻¹ than the lowest-energy conformation of the TS for R3b, which indicates that the contribution of channel R3b to the overall rate constant for R3 is negligible until very high temperatures; thus, we omit this channel in the present article.

The barrier height and reaction energy for R3a calculated at both the M06-2X/MG3S and CCSD(T)-F12a/cc-pVTZ-F12//M06-2X/MG3S + CV + R levels of theory are summarized in Table 5. These energetics were calculated using the lowest-energy conformations for the species in which multiple conformations are possible. Table 5 shows that the two-point CBS-extrapolation scheme based on CCSD(T) with cc-pVTZ and cc-pVQZ basis sets and the CCSD(T)-F12a/cc-pVTZ-F12 calculations lead to similar results for both the reaction energy and the barrier height for R3a. Because of the more rapid convergence with respect to basis set, explicitly correlated CCSD(T)-F12 methods paired with a triple- ζ basis set have been shown to achieve a level of accuracy that is often even better than that achieved through conventional CCSD(T) calculations employing a quintuple-zeta basis set.^{43,44} Thus, while our results based on conventional CCSD(T) and explicitly correlated CCSD(T)-F12 are in close agreement (Table 5), we have elected to use the CCSD(T)-F12a/cc-pVTZ-F12 method—which is also computationally less demanding—to approximate the CBS-limit for the energetics of the present reaction system, which we denote and use as the “best estimate” of the true CCSD(T)/CBS result for all

subsequent discussions. In addition, Table 5 also shows that the core–valence and scalar relativistic effects are negligible for this reaction system, contributing less than 0.2 kJ mol⁻¹ to the energetics of interest.

The zero-point-exclusive barrier height ($V_f^\ddagger$) computed in this study via the CCSD(T)/CBS//M06-2X/MG3S + CV + R method has a value of 68.16 kJ mol⁻¹, which is in excellent agreement with the value of 67.91 kJ mol⁻¹ computed in the study by Voegele et al.⁸ using G3B3 theory. To the best of our knowledge, the study by Voegele et al. seems to be the only other study to have characterized the TS for R3a (conversely, we note that several computational investigations have been conducted on the energetics of channel R3b).^{4–8} With all other things being equal, the small difference between the barrier height reported in this study for R3a and that obtained via G3B3 by Voegele et al. will lead to a rate constant that is only about 10% smaller than that obtained by Voegele et al. at 298.15 K. The geometry for the lowest-energy TS structure in R3a is also in reasonable agreement between the two studies, despite the fact that the M06-2X hybrid meta-GGA density functional has recently been shown⁴² to generally predict the internuclear distances in transition states more accurately than B3LYP. The barrier height calculated with M06-2X/MG3S for R3a is 60.68 kJ mol⁻¹, which is reasonable given the uncertainty of about 8.4 kJ mol⁻¹ (~ 2 kcal mol⁻¹) generally ascribed to M06-2X with a triple- ζ caliber basis set. We note that the B3LYP/6-31G(d) results reported by Voegele et al. indicate that the barrier height for R3a is significantly underestimated at that level of theory ($V_f^\ddagger = 42.38$ kJ mol⁻¹).

The zero-point-exclusive reaction energy for R3, ΔE , and its zero-point-inclusive analogue reaction enthalpy at 0 K, ΔH_0° , were computed to be -46.35 and -35.06 kJ mol⁻¹, respectively, using CCSD(T)/CBS//M06-2X/MG3S + CV + R (Table 5). The latter of these is in good agreement with the value of -34.31 ± 0.43 kJ mol⁻¹ derived from the experimental values listed at the ATcT for the enthalpies of formation at 0 K of N_2O_5 , H_2O and HNO_3 (which have respective values of 24.33 ± 0.35 kJ mol⁻¹, -238.919 ± 0.027 kJ mol⁻¹, and -124.45 ± 0.18 kJ mol⁻¹). The M06-2X/MG3S calculations underestimate the reaction enthalpy at 0 K for R3 by ~ 16 kJ mol⁻¹, which is outside the error margin expected for this level of theory. On the other hand, Hanway and Tao⁴ showed that MP2/6-31+G(d) significantly overestimates the experimental

value for ΔH_0° ; in addition, B3LYP with the same double- ζ basis set underestimates this quantity, and B3LYP with the 6-311++G(d,p) triple- ζ basis set is more accurate (−8.53, −41.46, and −33.76 kJ mol^{−1}, respectively).⁴

Because tunneling within the SCT approximation cannot occur at energies below the value of the V_a^G for the reactants when the reaction proceeds in the exergonic reaction, which is the case for R3, the underestimation of M06-2X/MG3S with regard to the reaction energy is not so important when only the forward reaction is considered. However, the reaction barrier height is critical since the quasiclassical rate constant and the tunneling correction are highly sensitive to this quantity. In this work, we improve the accuracy of M06-2X/MG3S with regard to the barrier height by scaling the V_{MEP} obtained with M06-2X/MG3S by a factor of 1.123, which is the ratio of the barrier height computed with CCSD(T)/CBS//M06-2X/MG3S + CV + R to that computed with M06-2X/MG3S, by using the VSCALE keyword in POLYRATE. The ensuing V_{MEP} and ΔV_a^G used in the calculation of $k^{\text{MS-CVT/SCT}}$ were gradually extended in both directions until convergence was observed for the rate constants at the temperatures of present interest (180–1800 K), which occurred at $s = \pm 2.0$ Å. The V_{MEP} and V_a^G profiles (where ΔV_a^G is the V_a^G minus the total ZPE for the reactants) calculated in this study for R3a are depicted in Figure 3.

Figure 3. Potential energy along the minimum energy path, $V_{\text{MEP}}(s)$ (black line), and ground-state vibrationally adiabatic potential curve, ΔV_a^G (red line, higher peak), calculated for R3 using M06-2X/MG3S and scaled to reproduce the CCSD(T)/CBS//M06-2X/MG3S + CV + R barrier height.

3.4. Kinetics of Hydrolysis. The thermal rate constants for R3a computed over the temperature range 180–1800 K using MS-CVT/SCT are reported in Table 6, and can be summarized by the following modified Arrhenius expression:

$$k_{3a} = 9.51 \times 10^{-17} \left(\frac{T}{298\text{K}} \right)^{3.354} e^{-7900\text{K}/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (12)$$

The 0.27 kJ mol^{−1} difference between the barrier height computed with CCSD(T)-F12a/cc-pVTZ-F12 and that computed via the 2-point extrapolation for R3a (Table 4), and rough measures of the uncertainties in the ZPEs of the reactants and the TS—estimated through similar considerations as discussed in section 3.1—can be used to place a lower

Table 6. Thermal Rate Constants in cm³ molecule^{−1} s^{−1} for R3a

<i>T</i> (K)	$k^{\text{CVT/SCT}}$	$k^{\text{MS-CVT/SCT}}$
180	4.75×10^{-36}	1.49×10^{-36}
200	5.54×10^{-34}	1.72×10^{-34}
250	3.26×10^{-30}	1.00×10^{-30}
298.15	9.61×10^{-28}	3.02×10^{-28}
300	1.15×10^{-27}	3.62×10^{-28}
400	2.01×10^{-24}	6.90×10^{-25}
600	4.45×10^{-21}	1.89×10^{-21}
800	2.52×10^{-19}	1.30×10^{-19}
1000	3.20×10^{-18}	1.97×10^{-18}
1200	1.90×10^{-17}	1.37×10^{-17}
1500	1.26×10^{-16}	1.11×10^{-16}
1800	4.91×10^{-16}	5.16×10^{-16}

bound on the 2σ uncertainty in the rate constant obtained via eq 12. Through this analysis, we obtain an uncertainty factor of approximately 1.23 in the computed rate constant at 298 K.

Also listed in Table 6, for comparison, are the CVT/SCT rate constants calculated for R3a. At the lowest temperature considered in this study, 180 K, the tunneling contribution calculated using the SCT model is a factor of 2.60, which decreases to a factor of 1.35 by 298 K. These results are in good agreement with the calculations of Voegelé et al., who also employed the SCT model to capture the tunneling through a potential computed using the G3B3 composite method.⁸ The k_3 value computed by Voegelé et al. at 298 K via CVT/SCT without correcting for hindered rotations is 5.4×10^{-28} cm³ molecule^{−1} s^{−1}. This value is in accord with the CVT/SCT rate constant of 9.6×10^{-28} cm³ molecule^{−1} s^{−1} obtained at 298 K in the present study.

As mentioned in section 3.2, four structures were located for the transition state of R3a (Figure 1). These four structures seem to be roughly interconnected via combinations of highly constrained internal rotation around the breaking O–H partial bond in H₂O (or the forming O–N partial bond) and ring-flipping. A similar transition state was characterized recently for the dehydration of isobutyl alcohol,⁶⁴ and explicitly accounting for the torsional effects along the analogous O–H partial bond of H₂O in that system as opposed to not treating the torsional conformers as interconnected (i.e., approximating their partition functions from local harmonic treatments in light of the potentially large barriers associated with constrained torsional rotation) was found to lead to a negligible difference (of less ~5% at all temperatures presently considered). Because of the ring-like geometries of the TS conformers for R3a, we assume that torsional motions in these systems are highly constrained, such that the ensuing MS-T partition function is essentially just a conformational average of the “local” partition functions for each of the conformers. This treatment is sometimes referred to as multistructural local-harmonic (MS-LH), which, as explained in section 2.1, is obtained by setting all of the $f_{j,r}$ and Z_j factors equal to unity in eq 1. As was already noted in the case of N₂O₅, this anharmonic correction due to conformationally averaging over all structures dominates the torsional anharmonicity, and it is quite reasonable to expect the extent of this domination to further increase in the TS given its highly constrained torsions.

Following the MS-T convention, we have labeled the TS structures using the indices $j = 1$ –4 in Figure 1. Of these four, only the lowest-energy structure $j = 1$ was mentioned in the

study of Voegelé et al. The MS-LH F -factors for the TS, given in Table 1, show the expected behavior, namely that the two isoenergetic nonsuperposable mirror images comprising the lowest-energy structures in the set make the dominant contributions to the overall partition function at low to intermediate temperatures, with the contributions from the remaining two structures becoming increasingly important with increasing temperature. Both sets of structures make roughly equal contributions by about 900 K, after which point the contributions from the higher energy structures become increasingly more dominant due to differences between the moments of inertia and vibrational structure. Overall, the computed F -factors for the TS of R3a reveal that the anharmonic effects in this species, computed here within the context of the MS-LH approximation, increase its overall partition function by a factor that gradually increases from its value of 2.05 at 180 K to 5.20 by 1800 K.

Combining the total F -factors for the TS and N_2O_5 ($F_{\text{TS}}^{\text{MS-LH}}$ and $F_{\text{N}_2\text{O}_5}^{\text{MS-T}}$, respectively) as shown in eq 8 leads to the total reaction F -factor for R3, $F_{\text{R3}}^{\text{MS-T}}$, which is also given in Table 1. Because all of the torsional conformers of N_2O_5 are accessible at low temperatures and the torsions in this molecule are not constrained like they are in the ring-like TS, the F -factor for N_2O_5 is larger than that for the TS until very high temperatures. Consequently, our computations reveal that, at all but the highest temperature considered in our kinetic analysis, the rate constant for R3a is *decreased* when the overall effects of torsional anharmonicity in this reaction system are considered, with $F_{\text{R3}}^{\text{MS-T}}$ not reaching a value greater than 1 until temperatures in excess of about 1800 K. The most significant decrease in the rate constant is roughly a factor of 3, which persists over the temperature range of 180–400 K. This is in stark disagreement with the findings of Voegelé et al., where the anharmonicity in this reaction system was reported to increase the rate constant at 298 K by 3 orders of magnitude. In light of the torsional features of N_2O_5 and the TS for R3a, the proposal that the torsional correction for the TS could not only be larger than that for N_2O_5 , but ~ 1000 times larger even at room temperature, is difficult to justify. In the work of Voegelé et al., torsional anharmonicity was modeled using separable-torsion approximations,^{21,65–69} which can be reasonable when torsions are not extensively coupled to each other and/or to external rotation like they are in the reaction system under present investigation.

Overall, after accounting for torsions, the rate constant for the hydrolysis reaction reported by Voegelé et al., $5.2 \times 10^{-25} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, is nearly 2000 times larger than the value of $3.0 \times 10^{-28} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ we obtained in the present study via MS-CVT/SCT. This has important ramifications, as it indicates that when the effects of torsional anharmonicity are treated more comprehensively, their cumulative effect is to actually *decrease* the thermal rate constant and therefore *increase* the discrepancy between the computed rate constant for hydrolysis at 298 K and the experimental value reported by Wahner et al. ($2.5 \times 10^{-22} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). Thus, while the MS-T calculations performed in this work show that torsions are certainly important in this reaction system, they also place significant doubt on the hypothesis that torsional anharmonicity, if properly accounted for, can resolve the discrepancy between the computed and measured rate constants for the hydrolysis of N_2O_5 at atmospherically relevant temperatures.

4. CONCLUSIONS

New estimates for the thermochemistry of N_2O_5 and the thermal rate constants for its hydrolysis reaction were derived using multistructural partition functions that properly account for the anharmonic effects brought about by the torsions in these reaction systems. Our computational investigation revealed that three conformers (or structures) are generated by the two coupled torsions in N_2O_5 , and that by accounting for the coupling between these torsions as well as their coupling to external rotation, the MS-T torsional model employed to calculate anharmonic partition functions in this work led to the derivation of accurate thermochemistry for this species. In particular, the $S^\circ_{298.15}$ value for N_2O_5 computed in this study using MS-T partition functions is in very good agreement with experiment, and further supports the recommendations of Gurvich et al.⁵⁸ and NASA-JPL⁶⁰ over that listed at JANAF.⁵⁶ A subsequent third law analysis based on this computed entropy value and the equilibrium constant measurements of Osthoff et al.¹³ for $\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5$ led to the derivation of an experimentally based value for $\Delta_f H^\circ_{298.15}(\text{N}_2\text{O}_5)$ which is also in agreement with the Gurvich et al.⁵⁸ and NASA-JPL⁶⁰ recommendations, and with the value listed at ATcT;⁵⁵ however, it is about 3 kJ mol^{-1} higher than that from JANAF.⁵⁶ Finally, the computed thermal rate constant for the hydrolysis of N_2O_5 at 298.15 K—which in this work was obtained using multistructural canonical variational transition state theory with multidimensional tunneling—was found to be 3 orders of magnitude smaller than that previously reported by Voegelé et al., and this disagreement was shown to stem from the two different torsional models employed in these two works. On the basis of our MS-T calculations, which mark the most extensive treatment of the coupled torsions in this reaction system to date, we conclude that the torsional anharmonicity in this system cannot account for the 6-order-of-magnitude discrepancy between the computed and measured rate constant for the hydrolysis of N_2O_5 at 298.15 K. The extremely small rate constant computed for hydrolysis is in line with the suggestion by Brown et al.³ that the laboratory value for k_3 may be too high.

■ ASSOCIATED CONTENT

● Supporting Information

Geometrical parameters, graphical depictions, and vibrational frequencies for all structures of the reactants, transition state, and products for reaction R3 optimized with M06-2X/MG3S, thermochemistry for eq R2, and absolute CCSD(T)/cc-pVTZ, CCSD(T)/cc-pVQZ, and CCSD(T)-F12a/cc-pVTZ-F12 energies for all structures of the reactants, transition state, and products for reaction R3 optimized with M06-2X/MG3S. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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