

# A multifacet mechanism for the OH+HNO<sub>3</sub> reaction: An *ab initio* molecular orbital/statistical theory study

W. S. Xia<sup>a)</sup> and M. C. Lin<sup>b)</sup>

Department of Chemistry, Emory University, Atlanta, Georgia 30322

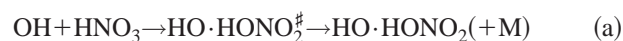
(Received 21 August 2000; accepted 10 November 2000)

The mechanism for the OH+HNO<sub>3</sub> reaction has been studied by *ab initio* molecular orbital calculations at the G2M(cc3) level of theory. Four complexes and four transition states have been found and confirmed by intrinsic reaction coordinate analyses. The commonly assumed six-membered ring complex formed by hydrogen bonding of the OH radical with HNO<sub>3</sub>, –ON(O)OH...OH–, was found to be stable by 8.1 kcal/mol; its decomposition producing NO<sub>3</sub>+H<sub>2</sub>O was predicted to have a barrier of 11.6 kcal/mol. A five-membered ring complex, –ON(O)OH...O(H)–, with the H atom of the OH radical placed out of the ring plane, was found to have a stability of 5.3 kcal/mol; it fragments to form NO<sub>3</sub>+H<sub>2</sub>O with a barrier of 6.6 kcal/mol. Two additional complexes, which are the mirror image of each other with a 7.4 kcal/mol binding energy, were found to be related to the OH exchange reaction with a 13.3 kcal/mol barrier above the complexes. The direct abstraction process producing H<sub>2</sub>O<sub>2</sub> and NO<sub>2</sub> was predicted to have a large barrier of 24.4 kcal/mol, insignificant to atmospheric chemistry. The rate constant has been calculated at 200–1500 K and 0–760 Torr. The results show that the reaction has strong pressure and tunneling effects below room temperature. In addition, the rate constants for the decay of OH and OD (in OD+DNO<sub>3</sub>) evaluated by kinetic modeling compare reasonably well with experimental data below room temperature. The unusually pronounced kinetic isotope effect observed experimentally,  $k_H/k_D \geq 10$ , could be accounted for by the combination of the greater tunneling rate in the H system and the large redissociation rate of stabilized complexes in the D system. The rate constant predicted for the production of H<sub>2</sub>O and NO<sub>3</sub> in the temperature range 750–1500 K can be effectively represented by the expression  $k = 1.45 \times 10^{-23} T^{3.5} \exp(+839/T) \text{ cm}^3/\text{s}$ . © 2001 American Institute of Physics. [DOI: 10.1063/1.1337061]

## I. INTRODUCTION

The reaction of the hydroxyl radical with nitric acid is of great importance to the chemistry of both stratosphere and troposphere.<sup>1</sup> It is also critical to the combustion of energetic materials, such as ammonium perchlorate and ammonium dinitramide,<sup>2</sup> occurring at high temperatures where only limited kinetic data are available.<sup>3</sup>

In the temperature region of interest to atmospheric chemistry, there have been many studies on the effects of temperature<sup>4–24</sup> and pressure.<sup>5,17,19,21,24</sup> The observed strong negative temperature effect and the presence of a noticeable pressure dependence below room temperature suggest the direct involvement of a long-lived association complex, HO·HONO<sub>2</sub>. A quantum chemical calculation on this long-lived complex was recently given by Aloisio and Francisco<sup>25</sup> and a theoretical analysis of low-temperature data has been made by Benson and co-workers<sup>18</sup> on the basis of the mechanism:



where “#” denotes internal excitation.

The formation of the abstraction products, H<sub>2</sub>O+NO<sub>3</sub>, has been confirmed experimentally at room temperature by Jourdain *et al.*<sup>11</sup> and Ravishankara and co-workers,<sup>15</sup> with unit product yield, [NO<sub>3</sub>]/[OH]<sub>0</sub>=1.0. This result suggests that the barrier for H abstraction by OH lies near the reactants and that the alternative slightly exothermic reaction,



if it occurs at all, is unimportant near room temperature.

The objective of the present study is to elucidate the mechanism for the reaction by fully characterizing the potential energy surface of the system, employing high-level *ab initio* molecular orbital methods to calculate the energies and molecular structures of the reactants, association complexes, and transition states involved in the reaction. These critical parameters are essential for prediction of rate constant calculations using appropriate statistical theories for a wide range of temperature and pressure. The result of this detailed *ab initio* molecular orbital study and the rate constant calculation are presented herein.

<sup>a)</sup>Permanent address: State Key Lab. for Phys. Chem. of Solid Surfaces, Institute of Phys. Chem. and Dept. of Chem., Xiamen University, Xiamen, 361005, P.R. China.

<sup>b)</sup>Electronic mail: chemmcl@emory.edu

## II. COMPUTATIONAL METHODS

### A. *Ab initio* calculation

The geometries of the reactants, products, complexes, and transition states have been optimized at the hybrid density functional B3LYP method<sup>26</sup> with the 6-311G(*d,p*) basis set.<sup>27</sup> Vibrational frequencies calculated at the same level of theory were employed to characterize stationary points and zero-point energy (ZPE) corrections. All the stationary points have been positively identified for local minima with the number of imaginary frequencies NIMAG=0 and for transition states with NIMAG=1. In order to confirm that a specific transition state connects the designated local minima, we also performed intrinsic reaction coordinate (IRC) calculations<sup>28</sup> at the B3LYP/6-311G(*d,p*) level of theory.

To obtain more reliable energies of various species on the potential energy surface (PES), we used the G2M method,<sup>29</sup> which approximates RCCSD(T)/6-311+G(3*df*,2*p*) using a series of single-point calculations with the B3LYP optimized geometries for basis set size expansion, correlation energy, and systematic error corrections. This method performs well for open shell systems. Several versions of the scheme have been suggested by Mebel *et al.*<sup>29</sup> for varying molecular sizes. For the present system with five heavy atoms, G2M(cc3) was employed throughout. The method is briefly summarized as follows.

The total energy in G2M(cc3) is calculated with

$$E[\text{G2M(cc3)}] = E_{\text{bas}} + \Delta E(+ ) + \Delta E(2df) + \Delta E(\text{cc}) \\ + \Delta' + \Delta E(\text{HLC}) \\ + \text{ZPE}[\text{B3LYP/6-311G}(d,p)],$$

where

$$E_{\text{bas}} = E[\text{PMP4/6-311G}(d,p)], \\ \Delta E(+ ) = E[\text{PMP4/6-311+G}(d,p)] \\ - E[\text{PMP4/6-311G}(d,p)], \\ \Delta E(2df) = E[\text{PMP2/6-311G}(2df,p)] \\ - E[\text{PMP2/6-311G}(d,p)], \\ \Delta E(\text{cc}) = E[\text{CCSD(T)/6-311G}(d,p)] \\ - E[\text{PMP4/6-311G}(d,p)], \\ \Delta' = E[\text{MP2/6-311+G}(3df,2p)] \\ - E[\text{MP2/6-311G}(2df,p)] \\ - E[\text{MP2/6-311+G}(d,p)] \\ + E[\text{MP2/6-311G}(d,p)].$$

The empirical “higher level correction” is given by

$$\Delta E(\text{HLC}) = 0.001(-5.63n_{\beta} - 0.19n_{\alpha}) \quad \text{for open shell}$$

and

$$\Delta E(\text{HLC}) = 0.001(-5.45n_{\beta} - 0.19n_{\alpha}) \\ \text{for closed shell,}$$

where  $n_{\alpha}$  and  $n_{\beta}$  are the numbers of  $\alpha$  and  $\beta$  valence electrons, respectively. All calculations were carried out with GAUSSIAN 94 programs.<sup>30</sup>

### B. Statistical theory calculation

On the basis of the reaction energetics predicted by the G2M method as described previously, we performed microcanonical variational Rice–Ramsperger–Kassel–Marcus calculations for the individual product channels with the VARIFLEX code<sup>31</sup> to be compared with experimental data. The variational treatment in VARIFLEX is similar to the variational transition state theory (VTST) approach.<sup>32</sup> A detailed review on VTST has been made recently by Truhlar *et al.*<sup>33</sup>

In the master equation calculation, the energy of a given molecule is divided into a contiguous set of grains. Each grain has the same width and contains a bundle of states which has a common, averaged energy,  $E_i$ , and a microcanonical rate coefficient  $k_i$ . The master equation describes the evolution of the grain populations,  $\rho_i$ . For our one-well system, the master equation takes the form

$$\frac{d\rho_i(t)}{dt} = \phi_i + \omega \sum_{j=1}^m P_{ij}\rho_j(t) - \omega\rho_i(t) - (k_{i1} + k_{i2})\rho_i(t), \quad (1)$$

where  $\phi_i$  represents the input rate from the incoming two fragments,  $m$  is the number of grains which is chosen such that the population of the  $m$ th grain contributes negligibly to the rate coefficient,  $\omega$  is the collision frequency (which is a function of temperature and pressure),  $k_{i1}(E)$  and  $k_{i2}(E)$  are the microcanonical rate coefficients for decomposition and redissociation, and  $P_{ij}$  the probability of energy transfer from grain  $j$  to grain  $i$  upon collision. A simple exponential-down model<sup>34</sup> was employed for  $P_{ij}$ :

$$P_{ij} = A_j \exp[-\alpha(E_j - E_i)], \quad j \geq i, \quad (2)$$

where  $\alpha$  is a parameter governing the efficiency of energy transfer;  $\alpha^{-1}$  corresponds to the average energy removed per collision for the down collision,  $\langle \Delta E \rangle_{\text{down}}$ .  $A_j$  are normalization constants obtained from the normalized condition:

$$\sum_i P_{ij} = 1. \quad (3)$$

The master equation was solved approximately with the modified strong collision model.<sup>34</sup>

For the loose, barrierless transition states, the Varshni potential,<sup>35</sup>

$$V(R) = D_e \{1 - (R_0/R) \exp[-\beta(R^2 - R_0^2)]\}^2 - D_e, \quad (4)$$

was employed to represent the potential along the reaction coordinate because it is more realistic than the Morse function when it is “flatter” at large  $R$ . In the above equation,  $D_e$  is the bond energy excluding zero-point vibrational energies;  $R$  is the reaction coordinate (i.e., the distance between the two bonding atoms in the present case) and  $R_0$  its equilibrium value.

In the variational transition state, the rovibrational modes are separated into conserved and transitional modes,<sup>36–38</sup>

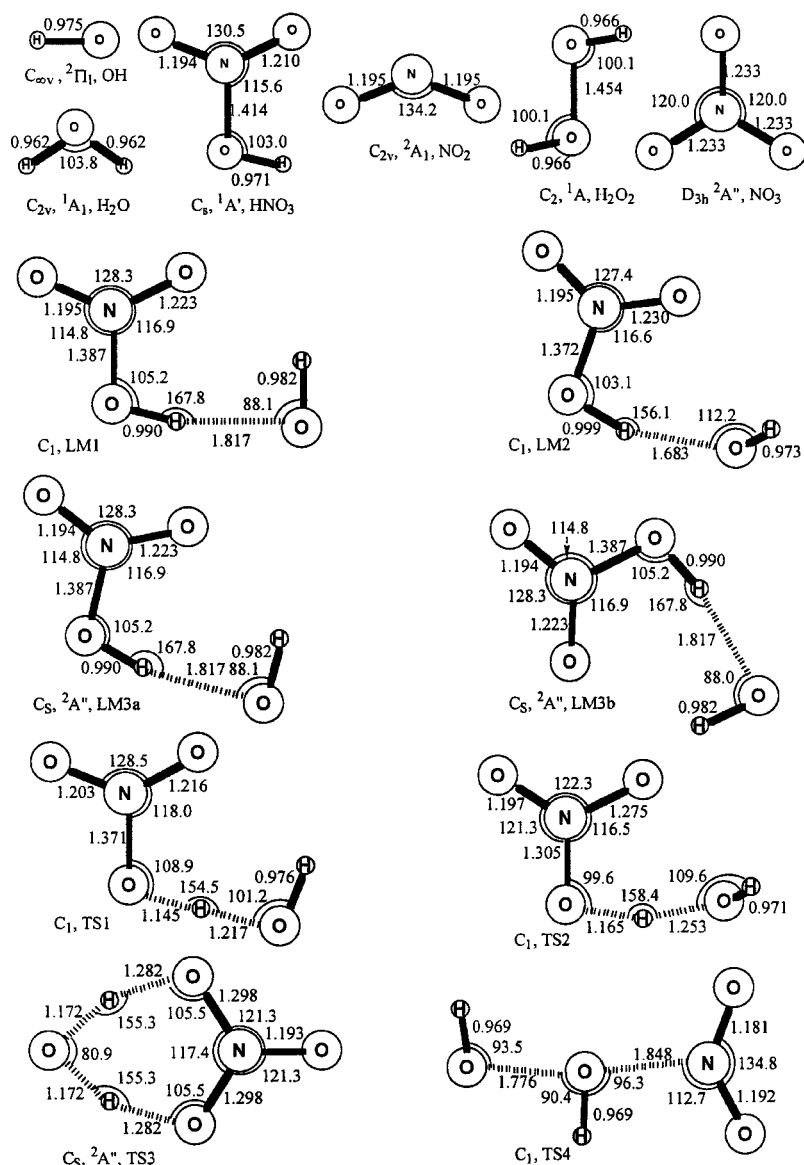


FIG. 1. The structures and symmetry of all species involved in the reaction of OH with HNO<sub>3</sub> optimized at the B3LYP/6-311G(*d,p*) level.

$$Q_{\text{ts}}(R, T) = Q_{\text{cons}}(R, T) \cdot Q_{\text{tr}}(R, T), \quad (5)$$

$Q_{\text{cons}}(R, T)$  is the conserved mode partition function, and  $Q_{\text{tr}}(R, T)$  the transitional mode partition function. With this separation, one can evaluate the number of states by Monte Carlo integration for the convolution of the sum of vibrational quantum states for the conserved modes with the classical phase space density of states for the transitional modes. The classical treatment of the transitional modes has been shown to be accurate by comparing the result of a quantum treatment in a thermally averaged calculation of the high-pressure rate constant for the methyl radical recombination reaction.<sup>37,38</sup> In this treatment, a minimization of  $N_{EJ}$ , the energy  $E$  and total angular momentum  $J$  conserved number of available states, with respect to an assumed two bonding-atom separation on the reaction coordinate  $R$  is performed.

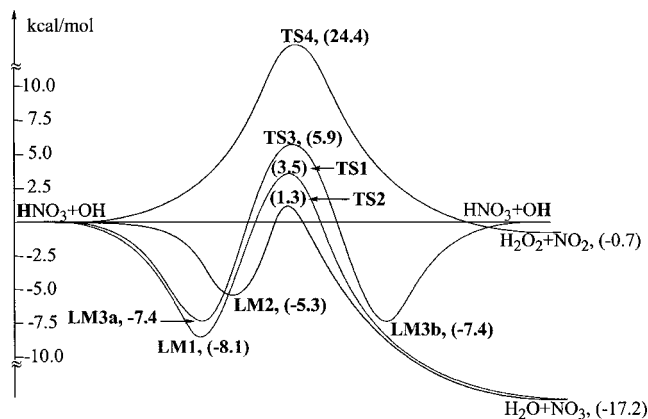
For a tight transition state, a rigid rotor harmonic oscillator calculation of  $N_{EJ}$  is employed with Eckart tunneling corrections, if necessary.<sup>31</sup>

### III. RESULTS AND DISCUSSIONS

#### A. Geometries, frequencies and orbital bonding analysis

*Geometries.* The optimized geometries of all species involved in the reaction (reactants, products, transition states, and corresponding complexes) are depicted in Fig. 1. Four transition states were found for the reaction. IRC calculations have confirmed that TS1 connects molecular complex 1 (or local minimal 1, denoted as LM1) formed by the association of OH with HNO<sub>3</sub> with the products NO<sub>3</sub>+H<sub>2</sub>O. Similarly, TS2 also connects LM2 with NO<sub>3</sub>+H<sub>2</sub>O. The transition state for the OH exchange reaction, TS3, connects the two equivalent complexes, LM3a and LM3b. TS4 is the transition state for the reaction OH+HNO<sub>3</sub>→H<sub>2</sub>O<sub>2</sub>+NO<sub>2</sub>. The potential energy surface (PES) profile of the entire system is presented in Fig. 2.

In LM1 and TS1, OH and HNO<sub>3</sub> form almost planar, six-membered ring structures with the key difference be-

FIG. 2. PES of the OH+HNO<sub>3</sub> reaction system.

tween the two in the apparent shortening of  $R(\text{HO}\dots\text{HNO}_3)$  from 1.817 to 1.217 Å and the decrease in the bond angle  $A(\text{OHO})$  by 13.3°. In TS1 the atoms in the ring also deviate farther from the planar structure. TS2 and LM2 effectively have five-membered ring structures, since the H atom in the OH radical is out of plane in both cases. TS2 differs from LM2 in a similar manner as in the TS1/LM1 case, with  $R(\text{HO}\dots\text{HNO}_3)$  decreasing from 1.683 Å in LM2 to 1.253 Å in TS2, but the  $A(\text{OHO})$  angle increases slightly by 2.3°.

Both LM1 and LM2 are the molecular complexes formed directly by the association of OH and HNO<sub>3</sub> through hydrogen bonding. As shown in Fig. 1,  $R(\text{HO}\text{---}\text{HNO}_3)$  is longer in LM1 than that in LM2 by 0.134 Å, while  $R(\text{O}\text{---}\text{H})$  in the HNO<sub>3</sub> fragment of LM1 is shorter than that of LM2 by 0.009 Å.  $R(\text{N}\text{---}\text{OH})$  in the HNO<sub>3</sub> of LM1 is longer than that of LM2 and, similarly,  $R(\text{O}\text{---}\text{H})$  of the OH radical fragment in LM1 is longer than the corresponding bond in LM2, which is attributable to the weak interaction of O...H and the bigger angles  $A(\text{NOH})$  and  $A(\text{OHO})$  in the six-membered ring of LM1. Moreover, the difference in bonding distance between N-OH and N-O in LM1 is greater than the difference in LM2, suggesting that LM1 is more similar to the reactants (HNO<sub>3</sub>+OH) than LM2 is. A search to connect LM1 with LM2 failed to find a transition state.

For TS1 and TS2, the difference in  $R(\text{N}\text{---}\text{OH})$  and  $R(\text{N}\text{---}\text{O})$  is smaller than that in LM1 and LM2, especially for TS2.  $R(\text{N}\text{---}\text{OH})$  in TS2 is shorter than that in TS1 by 0.066 Å, and  $R(\text{N}\text{---}\text{O}\text{---}\text{H})$  in TS2 is larger than that in TS1 by 0.020 Å, although  $R(\text{HO}\dots\text{HNO}_3)$  in TS2 is larger than the one in TS1, presumably caused by the larger stereo-repulsion between HNO<sub>3</sub> and OH in TS2; so TS2 is closer to the products (NO<sub>3</sub>+H<sub>2</sub>O) than TS1 is by comparing the geometry of the product pair.

TS3 appears to be a symmetric structure with  $C_s$  symmetry; it connects with hydrogen bonded complexes LM3a and LM3b, whose structures are very similar to that of LM1 except that the former have  $C_s$  symmetry, whereas the latter has  $C_1$  symmetry.

TS4 is the transition state of the OH radical attack on the O atom in the OH group of HNO<sub>3</sub> producing H<sub>2</sub>O<sub>2</sub>+NO<sub>2</sub>; its barrier is considerably larger than those of the aforementioned processes.

*Frequencies and orbital bonding analysis for complexes.*

In Table I, we have listed the frequencies and moments of inertia for all species involved in the reaction. For these complexes, the first vibrational frequencies ( $\nu_{ia}$ ) originate from the stretching mode of the OH radical fragment, and the second ( $\nu_{ib}$ ) from the OH stretching mode of the HNO<sub>3</sub> fragment. Both LM3a and LM3b have almost the same frequencies as LM1.

Comparing the  $\nu_{ib}$ 's of LM1 and LM2 with the OH stretching mode of the free HNO<sub>3</sub>, we find that those of LM1 and LM2 (3370 and 3187 cm<sup>-1</sup>, respectively) are smaller than that of HNO<sub>3</sub> (3735 cm<sup>-1</sup>) and that the one in LM1 is greater than that in LM2, reflecting the effects of the OH radical bonding with HNO<sub>3</sub> and a stronger HO...HNO<sub>3</sub> interaction in LM2 than LM1. However, LM2 has smaller bond angles than LM1; its stereo-repulsion energy is expected to be higher, so that the total energy of LM2 is higher than that of LM1. Comparing the  $\nu_{ia}$ 's of LM1 and LM2 with that of the free OH radical (3704 cm<sup>-1</sup>) indicates that the  $\nu_{ia}$  of LM1 (3621 cm<sup>-1</sup>) is smaller, whereas that of LM2 (3736 cm<sup>-1</sup>) with the out-of-plane H atom is larger. These results can be further understood by the bonding orbital analysis given in the following.

According to our analysis of the bonding orbitals (i.e., the electron densities of typical bonding orbitals, as shown in Fig. 3), the OH radical fragment in the six-membered ring of LM1 mainly interacts with the OH group in HNO<sub>3</sub> by the  $p_x$ ,  $p_y$ , and  $s$  orbitals (with the  $\sigma$  interaction on the  $xy$  molecular plane and the  $\pi$  orbital ( $p_z$ ) perpendicular to the plane). The  $\pi$  orbital interacts weakly with the HNO<sub>3</sub> by  $\pi$  bonding, shoulder to shoulder. For the five-membered ring LM2, the H atom of the OH radical is out of the ring plane, so the  $\sigma$  orbital (in this case  $s$  or  $p_z$ ) and, especially, the  $\pi$  orbital (in this case  $p_x$  or  $p_y$ ) can interact more strongly with O and OH of the HNO<sub>3</sub> fragment in LM2 by forming symmetry-adapted  $\sigma$ -bonding orbitals; accordingly, the OH stretching frequency of the OH radical in LM2 is closer to that of H<sub>2</sub>O.

Figure 3 indicates that LM1 and TS1 have an obvious six-membered ring bonding region between OH and HNO<sub>3</sub>, while LM2 and TS2 have a five-membered ring bonding region due to the out of plane geometry of the H atom of the hydroxyl radical fragment. In general, a stronger HO...HNO<sub>3</sub> bonding exists in the transition state than in the corresponding complex. In addition, TS2 has more bonding orbitals between the OH and HNO<sub>3</sub> fragments than TS1 and TS3 have; this is consistent with the lowest total energy of TS2 among all the transition states (see Fig. 2 and Table II).

Moreover, atomic spin density data show that in LM2 the OH radical interacts with the ring-O in HNO<sub>3</sub> [see also Figs. 3(a) and 3(b)], but in LM1 this interaction is negligibly small. The spin densities of the two entities O and OH of the OH radical fragment in LM1 are 1.035 and 1.010, respectively, whereas in LM2 they are 0.933 and 0.910, indicating again that the interaction of the OH with HNO<sub>3</sub> in LM2 is stronger and dominated by the  $\pi$ -orbital contribution. On the other hand, in LM1  $\sigma$ -orbital contribution from the OH radical fragment to the interaction between the reactants is predominant. Further orbital and atomic spin density analyses for the transition states indicate that  $\pi$  bonding interaction

TABLE I. Frequencies and moments of inertia for TS1, TS2, TS3, TS4, reactants, products, and complex (LM1, LM2, LM3a, LM3b) with the geometry optimized at the B3LYP/6-311G(*d,p*) level for OH+HNO<sub>3</sub> and OD+DNO<sub>3</sub> (denoted by D).

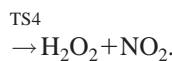
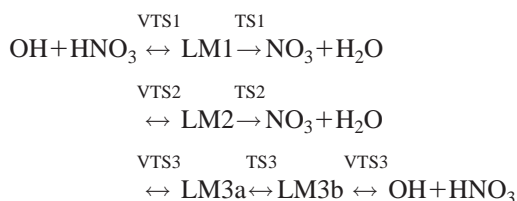
Species	$I_i$ (a.u.)	$\nu_j$ (cm <sup>-1</sup> )
OH	0.0, 3.2, 3.2	3704
OD	0.0, 6.1, 6.1	2698
HNO <sub>3</sub>	138.5, 149.7, 288.2	3735, 1778, 1359, 1327, 912, 777, 655, 589, 481
DNO <sub>3</sub>	139.0, 160.3, 299.3	2719, 1755, 1352, 1038, 911, 776, 651, 549, 356
H <sub>2</sub> O	2.3, 4.1, 6.4	3906, 3809, 1639
D <sub>2</sub> O	4.0, 8.2, 12.3	2862, 2747, 1199
NO <sub>3</sub>	130.2, 130.3, 260.5	1136, 1123, 1123, 802, 259, 258
H <sub>2</sub> O <sub>2</sub>	1456.4, 3780.9, 3782.1	3782, 3781, 1456, 1303, 943, 347
NO <sub>2</sub>	7.5, 138.3, 145.8	1705, 1399, 767
TS1	145.5, 549.4, 694.3	3685, 1682, 1502, 1304, 1248, 891, 784, 741, 671, 653, 405, 333, 153, 97, 1638( <i>i</i> )
TS1(D)	149.8, 569.6, 718.0	2683, 1656, 1312, 1107, 984, 880, 780, 683, 622, 551, 378, 250, 142, 97, 1188( <i>i</i> )
TS2	143.0, 475.9, 613.4	3764, 1764, 1575, 1427, 1399, 1020, 832, 790, 698, 600, 509, 508, 302, 124, 1259( <i>i</i> )
TS2(D)	147.8, 500.3, 638.3	2742, 1641, 1359, 1209, 1020, 1014, 829, 789, 695, 505, 439, 381, 291, 122, 953( <i>i</i> )
TS3	144.6, 490.4, 635.1	2082, 1693, 1585, 1297, 1282, 1025, 859, 814, 793, 766, 704, 521, 492, 125, 1437( <i>i</i> )
TS3(D)	148.8, 501.7, 650.5	1682, 1473, 1353, 1053, 1025, 957, 807, 794, 762, 652, 511, 508, 491, 127, 1059( <i>i</i> )
TS4	145.8, 749.6, 891.6	3790, 3782, 1803, 1378, 1177, 949, 782, 485, 409, 295, 287, 152, 132, 71, 705( <i>i</i> )
LM1	147.0, 624.1, 771.1	3621, 3370, 1762, 1453, 1333, 943, 785, 684, 662, 640, 500, 247, 202, 159, 77
LM1(D)	152.1, 641.6, 793.7	2636, 2463, 1726, 1338, 1108, 942, 783, 681, 603, 512, 380, 200, 187, 148, 83
LM2	147.5, 537.8, 680.3	3736, 3187, 1746, 1472, 1293, 946, 885, 783, 690, 633, 434, 347, 249, 152, 86
LM2(D)	153.6, 562.3, 707.5	2721, 2328, 1698, 1310, 1124, 945, 783, 687, 641, 600, 317, 269, 235, 151, 85
LM3a	147.0, 623.8, 770.8	3618, 3372, 1762, 1454, 1333, 943, 785, 684, 662, 640, 498, 249, 202, 159, 77
LM3b	147.0, 623.8, 770.7	3618, 3372, 1762, 1454, 1333, 943, 785, 684, 662, 640, 498, 248, 202, 159, 77
LM3(D)	152.1, 641.6, 793.7	2636, 2462, 1726, 1338, 1108, 942, 782, 680, 603, 503, 379, 200, 184, 147, 80

between OH and HNO<sub>3</sub> increases as the  $R(\text{HO}\dots\text{HNO}_3)$  distance decreases and the atoms in the rings in TS1 and TS2 deviate farther from the planar structures.

In the exchange reaction transition state TS3 with  $C_s$  symmetry, however, there is no significant  $\pi$  interaction between OH and HNO<sub>3</sub>; the interaction is dominated by  $\sigma$  bonding as shown in Fig. 3(c).

## B. PES and reaction mechanism

As listed in Table I, four complexes have been identified and confirmed by IRC calculations to be connected with the reactants, TSs, and products according to the following reaction scheme:



The corresponding PES of the system is presented in Fig. 2.

As presented in Table II, the G2M//B3LYP/6-311G(*d,p*) energies are close to the values predicted by CCSD(T)/6-311G(*d,p*)//B3LYP/6-311G(*d,p*). Actually we also tested G2M calculations with optimized geometry at the levels of B3LYP/6-311+G(*d,p*) and B3LYP/cc-pvdz; the results showed very small differences. As shown in Fig. 2, both complexes LM1 and LM2, which lie 8.1 and 5.3 kcal/mol, respectively, below the reactants through barrierless association, lead to the formation of the NO<sub>3</sub> and H<sub>2</sub>O products. The extra stability of LM1 over LM2, as alluded to before, results from the additional hydrogen bonding between the hydroxyl H atom and one of the terminal oxygen atoms of HNO<sub>3</sub> (see Fig. 1). A similar six-centered complex has recently been reported by Aloisio and Fransisco<sup>25</sup> with a 6.0 kcal/mol binding energy at the CCSD(T)/6-311++G(2*d*,2*p*)//B3LYP/6-311++G(2*d*,2*p*) level of theory. The penalty for the higher stability of LM1 is

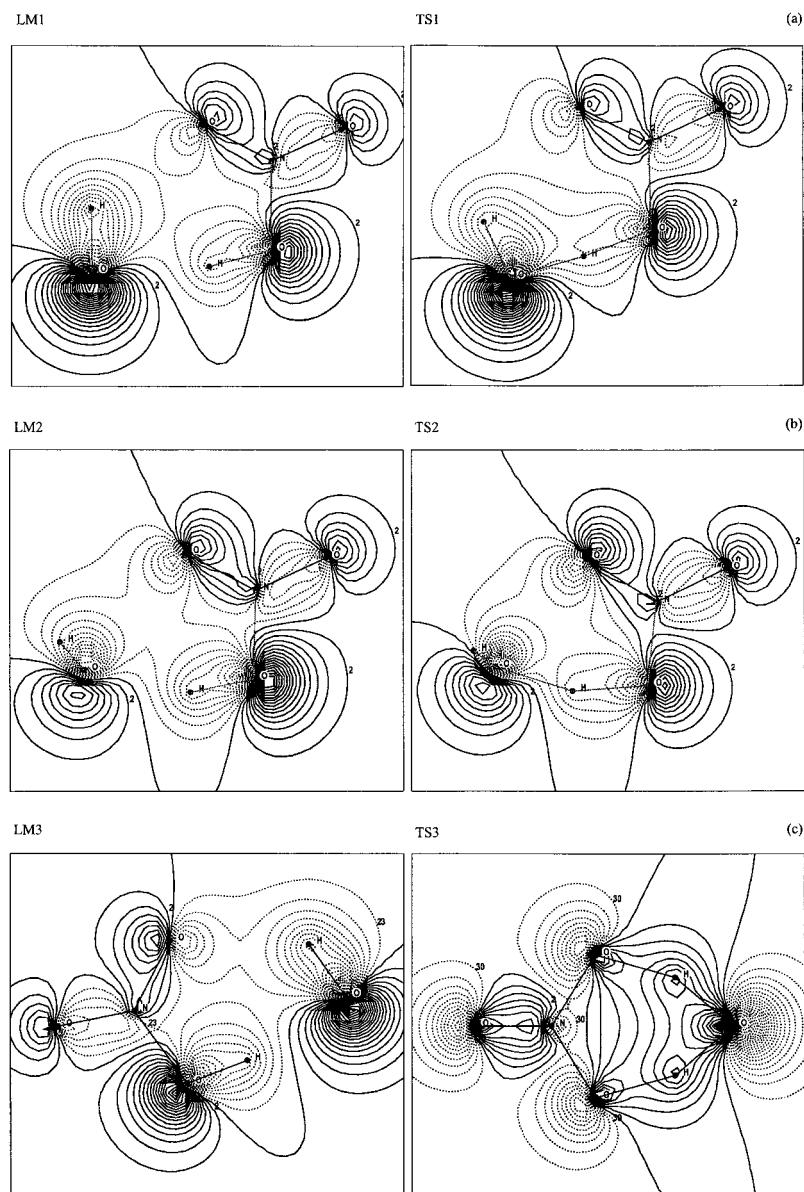


FIG. 3. Two-dimensional electron density contours at the level of B3LYP/6-311G(*d,p*) for some selected bonding orbitals of complexes and transition states. (a) LM1 and TS1; (b) LM2 and TS2; (c) LM3a or LM3b and TS3. The electron density is plotted in units of 0.025 electron bohr<sup>-3</sup>.

TABLE II. Energies of various species relative to the reactants with structures optimized at the B3LYP/6-311(*d,p*) level. [Energies in kcal/mol; R=HNO<sub>3</sub>+OH; P1=NO<sub>3</sub>+H<sub>2</sub>O; P2=NO<sub>2</sub>+H<sub>2</sub>O<sub>2</sub>; B1:6-311G(*d,p*); B2:6-311+G(3*df,2p*)].

Species	R	LM1	LM2	LM3a	LM3b	TS1	TS2	TS3	TS4	P1	P2
B3LYP/B1	0.0 <sup>a</sup>	-8.8	-8.4	-8.8	-8.8	-4.3	-7.5	2.6	16.8	-16.9	-1.4
ZPE(H)	0.0 <sup>b</sup>	1.7	1.9	1.4	1.4	-1.7	0.0	-1.8	0.3	-1.8	0.2
ZPE(D)	0.0 <sup>c</sup>	1.4	1.6	1.4	1.4	-1.0	0.3	-0.9		-1.9	
MP2/B1	0.0 <sup>d</sup>	2.5	-3.6	-7.2	-7.2	11.6	11.2	11.1	49.8	-23.9	-1.4
MP2/B2	0.0 <sup>e</sup>	1.0	-2.8	-5.8	-5.8	9.5	9.0	10.0	49.8	-27.5	-0.9
CCSD(T)/B1	0.0 <sup>f</sup>	-6.4	-4.5	-7.5	-7.5	5.7	4.3	7.7	25.8	-12.2	-0.6
G2M(cc3)(H)	0.0 <sup>g</sup>	-8.1	-5.3	-7.4	-7.4	3.5	1.3	5.9	24.4	-17.2	-0.7
G2M(cc3)(D)	0.0 <sup>h</sup>	-8.4	-5.6	-7.4	-7.4	4.2	1.7	6.9		-17.2	

<sup>a</sup>-356.687 008 a.u.

<sup>b</sup>21.9 kcal/mol.

<sup>c</sup>18.3 kcal/mol.

<sup>d</sup>-355.850 591 a.u.

<sup>e</sup>-356.073 812 a.u.

<sup>f</sup>-355.891 330 a.u.

<sup>g</sup>-356.201 894 a.u.

<sup>h</sup>-356.207 617 7 a.u. (H) for OH+HNO<sub>3</sub> and (D) for OD+DNO<sub>3</sub>.

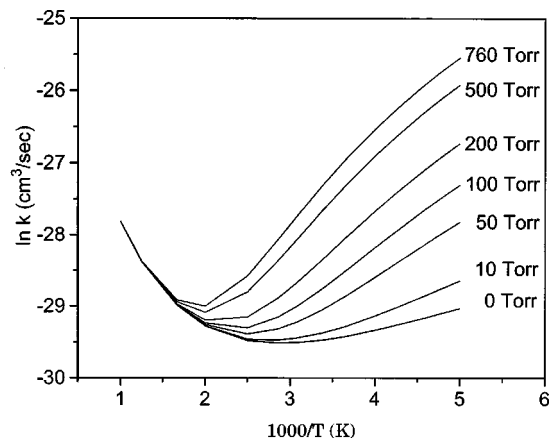


FIG. 4. Total rate constant calculated with VARIFLEX as a function of temperature ( $T=200\text{--}1000\text{ K}$ ) and pressures ( $P=0\text{--}760\text{ Torr}$ ) with  $\text{N}_2$  as bath gas.

the greater reaction barrier at TS1, 11.6 kcal/mol at the G2M(cc3) level, for  $\text{H}_2\text{O}$  elimination, compared with a smaller barrier at TS2, 6.6 kcal/mol, for the corresponding process. The absence of hydrogen bonding for the hydroxyl H atom makes the radical more reactive as one would expect.

The OH exchange process takes place by a symmetrical PES via LM3a, TS3, and LM3b, with the two complexes being the mirror image of each other, lying 7.4 kcal/mol below the reactants. The exchange barrier lies 13.3 kcal/mol above both complexes. The selected bonding orbitals for the exchange process are shown in Fig. 3(c). The formation and fragmentation of the complexes occur barrierlessly without a well-defined transition state.

The overall enthalpy change for the  $\text{OH}+\text{HNO}_3 \rightarrow \text{H}_2\text{O}+\text{NO}_3$  reaction was predicted by G2M to be  $-17.2$  kcal/mol, which compares reasonably with the value,  $-16.9$  kcal/mol, by B3LYP/6-311G(d, p) (see Table II) and the experimental value,  $-18.1$  kcal/mol.<sup>39</sup>

The production of  $\text{H}_2\text{O}_2$  and  $\text{NO}_2$  via TS4 has a distinct and large barrier of 24.4 kcal/mol, with a small exothermicity ( $-0.7$  kcal/mol), to be compared with the experimental value of  $-1.9$  kcal/mol<sup>39</sup> and the B3LYP/6-311G(d, p) value,  $-1.4$  kcal/mol (see Table II). The large reaction bar-

rier effectively rules out its significance in atmospheric chemistry.

## C. Rate constant calculations and kinetic implications

### 1. VARIFLEX results on $P$ , $T$ and tunneling effects

In Table I, we list the required molecular parameters (moment of inertia and frequencies) for rate constant calculations with the VARIFLEX code<sup>31</sup> for the three reaction channels, including those for the  $\text{OD}+\text{DNO}_3$  reaction. The  $L$ - $J$  parameters used in these calculations are: for the  $\text{N}_2$ -complex collision,  $\sigma=3.98\text{ \AA}$ ,  $\epsilon/K=189$  and for the He-complex collision,  $\sigma=3.40\text{ \AA}$  and  $\epsilon/K=63$ . These parameters were estimated by assuming those for  $\text{HO}\cdot\text{HNO}_3$  to be approximately the same as the values employed for  $\text{HNO}_3$ .<sup>34</sup> The results shown in Fig. 4 indicate that the  $\text{OH}+\text{HNO}_3$  reaction exhibits strong negative-temperature and positive pressure effects below room temperature. Above 600 K, the pressure effect disappears completely as has been found experimentally. These results can be easily rationalized. (1) The association reaction is barrierless and the smallest exit barrier leading to  $\text{NO}_3+\text{H}_2\text{O}$ , 1.3 kcal/mol above the reactants, which cannot be overcome easily at low temperatures ( $T<300\text{ K}$ ), can be easily crossed over at higher temperatures. (2) The well depth of the most stable complex is 8.1 kcal/mol, which is responsible for most of the predicted pressure effect (see Table III), the complex is thus unstable above room temperature. Accordingly, the redissociation process back to the reactants becomes dominant as the reaction temperature increases, resulting in the negative temperature dependence. The reaction channels via TS1 and TS2 become competitive only at higher temperatures ( $T>500\text{ K}$ , for example).

The turning point of temperature from negative to positive in the Arrhenius plot depends upon the pressure; the lower pressures have lower turning points because of the reduced collisional deactivation rate.

Figure 5 compares the total decay rate constants for OH and OD predicted with and without tunneling corrections at two pressures. At the lower pressure, the tunneling effect on the  $\text{OH}+\text{HNO}_3$  reaction is strong, especially at lower temperatures; at the higher pressure the effect becomes smaller due to the greater deactivation rate, which reduces the vibra-

TABLE III. A typical set of individual rate constants employed in kinetic modeling at 250 K as functions of pressure (in Torr) with  $\text{N}_2$  as bath gas.<sup>a</sup>

T	P	R1	R2+	R2-	R3	R4	R5+	R5-	R6	R7+	R7-
OH+HNO <sub>3</sub>	10	4.01E-14	2.90E-14	2.03E+04	7.02E+04	1.42E-13	1.91E-15	5.17E+05	6.83E+06	9.45E-15	5.03E+04
	20	4.00E-14	5.78E-14	4.04E+04	7.30E+04	1.42E-13	3.81E-15	1.03E+06	9.80E+06	1.89E-14	1.00E+05
	50	3.99E-14	1.43E-13	1.00E+05	7.51E+04	1.42E-13	9.52E-15	2.58E+06	1.46E+07	4.70E-14	2.50E+05
	100	3.98E-14	2.84E-13	1.98E+05	7.59E+04	1.42E-13	1.90E-14	5.15E+06	1.84E+07	9.35E-14	4.97E+05
	200	3.96E-14	5.58E-13	3.90E+05	7.65E+04	1.41E-13	3.78E-14	1.03E+07	2.19E+07	1.86E-13	9.87E+05
	350	3.93E-14	9.58E-13	6.69E+05	7.68E+04	1.41E-13	6.58E-14	1.78E+07	2.42E+07	3.22E-13	1.71E+06
	500	3.91E-14	1.35E-12	9.42E+05	7.71E+04	1.41E-13	9.36E-14	2.54E+07	2.54E+07	4.56E-13	2.42E+06
	600	3.90E-14	1.60E-12	1.12E+06	7.72E+04	1.41E-13	1.12E-13	3.03E+07	2.59E+07	5.44E-13	2.89E+06
	760	3.88E-14	2.00E-12	1.40E+06	7.73E+04	1.41E-13	1.41E-13	3.83E+07	2.66E+07	6.84E-13	3.64E+06
900	3.87E-14	2.35E-12	1.64E+06	7.74E+04	1.40E-13	1.67E-13	4.52E+07	2.69E+07	8.06E-13	4.29E+06	
OD+DNO <sub>3</sub>	50	9.79E-16	1.33E-13	1.47E+05	2.08E+02	1.95E-14	1.28E-14	2.99E+06	5.46E+05	8.26E-14	3.77E+05
	500	9.74E-16	1.26E-12	1.39E+06	2.13E+02	1.94E-14	1.24E-13	2.91E+07	5.90E+05	8.00E-13	3.65E+06

<sup>a</sup>The rate constants are given in units of  $\text{cm}^3/\text{s}$ ; R2+ and R2- represent the forward and reverse rate constants for reaction 2.

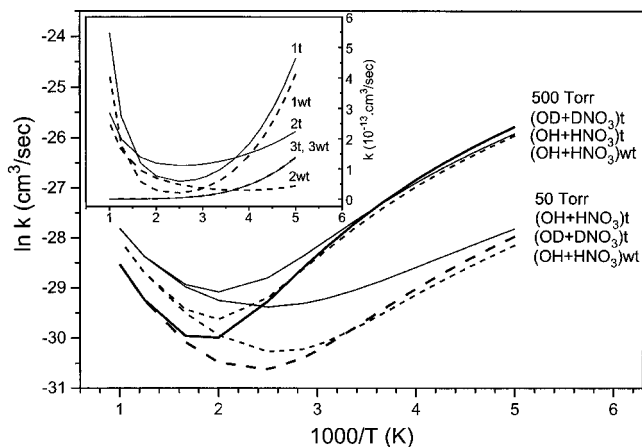
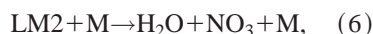
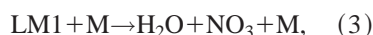


FIG. 5. Effects of tunneling on the rate constants calculated at 50 and 500 Torr for OH+HNO<sub>3</sub> and OD+DNO<sub>3</sub> using N<sub>2</sub> as bath gas. *t* and *w**t* indicate the results with and without tunneling corrections. Inset: Curves 1, 2 and 3 give the individual rate constants for channels 1, 2, and 3 at 50 Torr for OH+HNO<sub>3</sub>; solid curve: with tunneling corrections; dash curve: without tunneling corrections.

tional population of the excited complexes. In this system tunneling is significant because the energy barriers for the H-atom abstraction reactions lie 1–3 kcal/mol above the reactants. One would therefore expect a strong kinetic isotope effect enhanced by *P*-dependent quantum mechanical tunneling, in agreement with experiment results.<sup>23</sup>

## 2. Modeling of experimental data

On account of the thermal instability of the molecular complexes, kinetic modeling has to be carried out for the three main reactions in order to account for the experimentally observed OH decay kinetics. The modeling was performed with the following set of reactions:



The individual *T*, *P*-dependent rate constants for the above reactions were calculated with VARIFLEX; the values obtained for 250 K are listed in Table III for N<sub>2</sub> as buffer gas.

As shown in Fig. 6, the kinetically modeled result for 250 K at 50 Torr using N<sub>2</sub> as bath gas is in excellent agreement with the experimentally observed OH decay rates.<sup>24</sup> The apparent decay rate is much slower than the predicted total OH decay constant, excluding the redissociation of the deactivated molecular complexes in the simulation, suggesting that the contribution from the redissociation processes (R2-, R5-, and R7-) is very important. The statistical theory only predicts the probabilities for the formation of various products at *t*=0. In Fig. 6, the decay of OD in OD+DNO<sub>3</sub> under the same conditions was calculated with and without

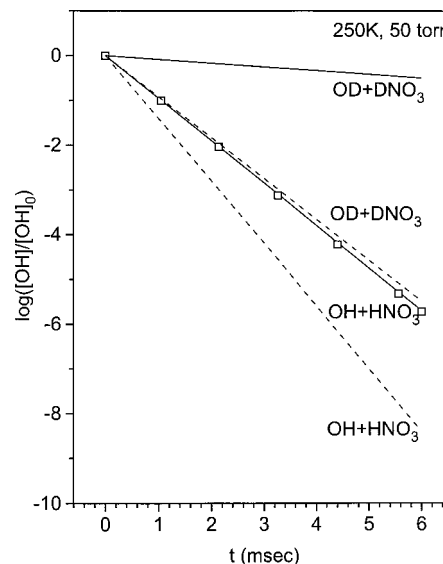


FIG. 6. Comparison of predicted OH(D) decay vs time at 250 K with 50 Torr pressure. Solid line: kinetically modeled decay using predicted rate constants; dash line: predicted decay excluding the redissociation of thermalized molecular complexes; data points: experimental data of Ref. 24 for OH+HNO<sub>3</sub> measured at 250 K and 50 Torr pressure with N<sub>2</sub> buffer gas (Ref. 24).

the inclusion of the redissociation of complexes back to the reactants. The implication of this significantly different result will be discussed in Sec. III C 3.

Figure 7 compares the predicted pressure effect with experimentally measured data<sup>24</sup> at three temperatures, 220, 250, and 296 K. The results of the kinetic modeling using the calculated individual rate constants agree well with experimental data.<sup>24</sup> These results also show that helium as a bath gas is less efficient than N<sub>2</sub> due to its lower energy transfer efficiency. At 296 K, the effect of pressure almost fully disappears, as was observed experimentally. The small deviations between the modeled and observed apparent OH decay constants may be accounted for by assuming temperature-

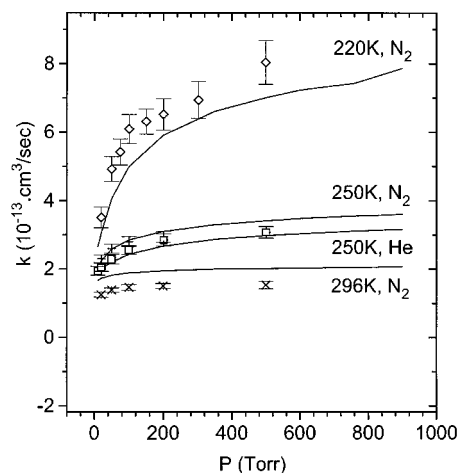


FIG. 7. Comparison of the predicted pressure effect on the apparent rate constants for OH decay at 220, 250, and 296 K using N<sub>2</sub> and He as bath gas. Solid curve: kinetically modeled values; data points: experimental results of Ref. 24.

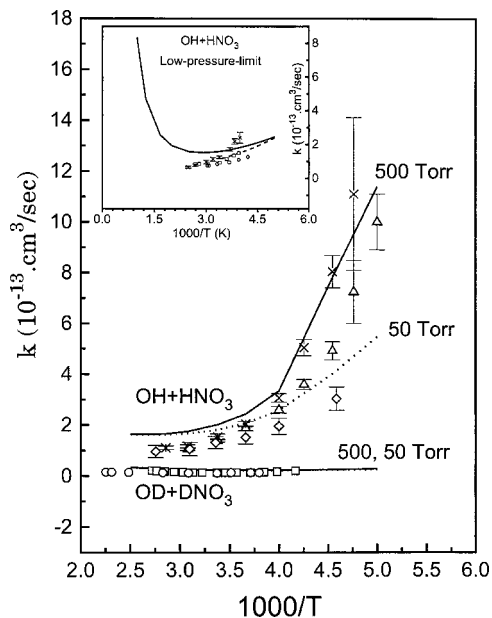


FIG. 8. Comparison of kinetically modeled OH(D)+H(D)NO<sub>3</sub> rate constants at 50 and 500 Torr. Dotted curve: result for 50 Torr; solid curve: result for 500 Torr. Experimental data for OH+HNO<sub>3</sub>: crosses, Ref. 24 for 500 Torr; diamond: Ref. 10 for 50 Torr; triangle: Ref. 24 for 50 Torr. For OD+DNO<sub>3</sub>, circle: Ref. 23; squares: Ref. 41. Inset: the low-pressure limit rate constant for OH+HNO<sub>3</sub>, solid curve: VARIFLEX result at 0 Torr; dashed line: Ref. 24; circle: Ref. 20; square: Ref. 16; cross: Ref. 11.

dependent energy transfer step size,  $\langle \Delta E \rangle_{\text{down}}$ . Due to the absence of  $\langle \Delta E \rangle_{\text{down}}$  parameters from experiment, in our calculations the energy transfer parameter  $\alpha$  was obtained by fitting the experimental data; 270 and 80 cm<sup>-1</sup> were used for N<sub>2</sub> and He as buffer gases, respectively.

The effect of temperature on the apparent second-order OH decay rate constant is shown in Fig. 8 for 50 and 500 Torr pressure. The predicted values agree reasonably well with experimental results obtained around these pressures. In the inset of Fig. 8, the predicted low pressure limit (calculated at  $P=0$  Torr) is compared with experimental results measured at  $P < 5$  Torr by different investigators. The agreement between theory and experiment is again quite reasonable in the temperature range where theory and experiment overlap. Also in Fig. 8, the rate constant determined for the OD+DNO<sub>3</sub> reaction is included for comparison. The apparent large kinetic isotope effect will be addressed later.

Kinetic modeling also allows us to confirm the finding of Jourdain *et al.*<sup>11</sup> and Ravishankara and co-workers<sup>15</sup> that the OH+HNO<sub>3</sub> reaction at room temperature occurs with unit product yield with  $[\text{NO}_3]/[\text{OH}]_0 = 1$ . Figure 9 shows the predicted decay of OH and the formation of NO<sub>3</sub> at 296 K. The concentration of NO<sub>3</sub> grows in concomitant with the decay of OH, rapidly approaching its unit yield with  $[\text{NO}_3]/[\text{OH}]_0 = 1$  as reported experimentally. Also included in Fig. 9 are the decay of OD and the formation of NO<sub>3</sub> predicted for the OD+DNO<sub>3</sub> reaction under the same conditions. This result will also be referred to later.

As alluded to previously, as the temperature of the system increases, the reaction becomes  $P$  independent and the decay of OH is dominated by the production of NO<sub>3</sub> and

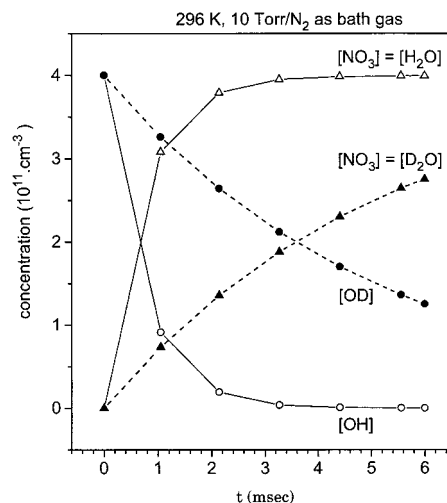


FIG. 9. Kinetically modeled OH(D) decay and NO<sub>3</sub> formation rates at 296 K.  $[\text{OH}]_0 = [\text{OD}]_0 = 4.00 \times 10^{11}$  molecules/cm<sup>3</sup>,  $[\text{HNO}_3] = [\text{DNO}_3] = 8.45 \times 10^{15}$  molecules/cm<sup>3</sup>;  $P = 10$  Torr, N<sub>2</sub> as buffer gas.

H<sub>2</sub>O. The rate constant evaluated at temperatures between 750 and 1500 K can be effectively represented by

$$k_{\text{NO}_3} = 1.45 \times 10^{-23} T^{3.5} \exp(+839/T) \text{ cm}^3/\text{s}.$$

Experimentally, only one value has been reported, by Glänzer and Troe<sup>40</sup> at 1000–1100 K with  $k_{\text{NO}_3} = 1.6 \times 10^{-13}$  cm<sup>3</sup>/s from the thermal decomposition of HNO<sub>3</sub> in shock waves. This result is about a factor of 7 lower than our predicted value given above. An improved experiment coupling pulsed laser photolysis with homogeneous shock heating is expected to provide more reliable kinetic data over a wider temperature range.

### 3. Kinetic isotope effect

The rate constant for the fully deuterated OD+DNO<sub>3</sub> reaction obtained by Singleton *et al.*<sup>23</sup> and Ravishankara and co-workers<sup>41</sup> is presented in Fig. 8 for comparison with those for the nondeuterated reaction. As shown in Fig. 8, the effect of isotope substitution is very large with  $k_{\text{H}}/k_{\text{D}} \geq 10$ , depending on the total pressure of the system, attributable to the strong  $P$  dependence of  $k_{\text{H}}$ .

The origin of such a large kinetic isotope effect and the apparent lack of pressure dependence in the OD decay kinetics cannot be understood without the benefit of kinetic modeling. In Fig. 5, the total rate constants including the formation of NO<sub>3</sub> and the collisional stabilization of the complex at 50 and 500 Torr for OH+HNO<sub>3</sub> and OD+DNO<sub>3</sub> predicted by the calculations with VARIFLEX, with and without tunneling corrections, are comparable. These results are in sharp contrast with the apparent OH and OD decay rate constants measured experimentally; they differ by as much as a factor of 10 or more as shown in Fig. 8. The apparent contradiction can be reasonably accounted for by kinetic modeling which includes the thermal decomposition of the collisionally stabilized association complexes producing NO<sub>3</sub>+H<sub>2</sub>O/D<sub>2</sub>O and the redissociation of the complexes back to the reactants. On account of the smaller barrier for NO<sub>3</sub> production, aided by the significant tunneling contribu-

tion, the OH+HNO<sub>3</sub> reaction producing NO<sub>3</sub> is much faster and its redissociation back to the reactants also occurs to a smaller extent than that in the OD+DNO<sub>3</sub> reaction (see Table III). This effect is clearly illustrated by the kinetically modeled results presented in Figs. 6 and 9 for the decay of OH/OD and the production of NO<sub>3</sub>+H<sub>2</sub>O/D<sub>2</sub>O under the same experimental conditions, employing the statistically predicted rate constants for reactions (1)–(7) (see Table III for  $T=250$  K).

It should note that since the reaction paths involve all coordinates, the one-dimensional Eckart tunneling correction is an approximation which, in principle, could be improved by performing multidimensional tunneling corrections with the inclusion of small curvature effects.<sup>42</sup>

#### IV. CONCLUSIONS

The mechanism for the OH+HNO<sub>3</sub> reaction has been elucidated with *ab initio* MO calculations at the G2M(cc3) level of theory. The reaction was found to occur by four distinct channels via four transition states (TSs) and four molecular complexes (LMs). Two of the reaction channels produce NO<sub>3</sub>+H<sub>2</sub>O via a five- and a six-membered ring LM with the TSs lie 1.3 and 3.5 kcal/mol above the reactants, respectively. The third channel, which results in the exchange of the OH group in HNO<sub>3</sub> with the attacking radical, takes place via two equivalent LMs with a binding energy of 7.4 kcal/mol and the isomerization barrier of 13.3 kcal/mol. The direct abstraction reaction producing NO<sub>2</sub>+H<sub>2</sub>O<sub>2</sub> was predicted to have a barrier of 24.4 kcal/mol, which makes the reaction too slow to be significant in atmospheric chemistry.

The formation of all LMs occurs barrierlessly without well-defined transition states. By statistical theoretical calculations using the variable, flexible transition state approach and kinetic modeling for the decay of OH radicals, we can account for the experimentally observed positive pressure and negative temperature dependencies with strong tunneling effects. The results illustrate the importance of the redissociation of stabilized molecular complexes back to the reactants, which pronouncedly reduces the apparent OH decay rates measured experimentally.

The large kinetic isotope effect observed experimentally was concluded to result from the combination of the effects of mass, reaction barrier (due to ZPE corrections), quantum-mechanical tunneling, and the backdissociation of stabilized molecular complexes. The overall effect observed experimentally can only be understood by kinetic modeling with coupled reactions including the decomposition of stabilized complexes giving the NO<sub>3</sub>+H<sub>2</sub>O products as well as the reactants.

#### ACKNOWLEDGMENTS

This work was sponsored partly by Emory University and partly by the Caltech Multidisciplinary University Research Initiative under ONR Grant No. N00014-95-1-1338, Program Manager, Dr. Judah Goldwasser. The authors gratefully acknowledge useful discussions with Professor S. J. Klippenstein and Professor D. M. Wardlaw on the applica-

tion of the VARIFLEX program. The preliminary work of Dr. D. Chakraborty on LM1 and TS1 search is also appreciated.

- <sup>1</sup>R. P. Wayne, *Chemistry of Atmospheres*, 2nd ed. (Clarendon, Oxford, 1991).
- <sup>2</sup>J. Park, D. Chakraborty, and M. C. Lin, *27th International Combustion Symposium* (The Combustion Institute, Pittsburgh, 1998), p. 2351.
- <sup>3</sup>R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, and J. Troe, *J. Phys. Chem. Ref. Data* **21**, 1125 (1992).
- <sup>4</sup>D. Husain and R. G. W. Norrish, *Proc. R. Soc. London, Ser. A* **273**, 165 (1963).
- <sup>5</sup>C. Morley and I. W. M. Smith, *J. Chem. Soc., Faraday Trans. 2* **68**, 1016 (1972).
- <sup>6</sup>J. J. Margitan, F. Kaufman, and J. G. Anderson, *Int. J. Chem. Kinet.* **7**, 281 (1975).
- <sup>7</sup>I. W. M. Smith and R. Zellner, *Int. J. Chem. Kinet.* **1**, 341 (1975).
- <sup>8</sup>H. H. Nelson, W. J. Marinelli, and H. S. Johnston, *Chem. Phys. Lett.* **78**, 495 (1981).
- <sup>9</sup>P. H. Wine, A. R. Ravishankara, N. M. Kreutter, R. C. Shah, J. M. Nicovich, R. L. Thompson, and D. J. Wuebbles, *J. Geophys. Res. B* **86**, 1105 (1981).
- <sup>10</sup>W. J. Marinelli and H. S. Johnston, *J. Chem. Phys.* **77**, 1225 (1982).
- <sup>11</sup>J. L. Jourdain, G. Poulet, and G. Lebras, *J. Chem. Phys.* **76**, 5827 (1982).
- <sup>12</sup>B. Fritz, K. Lorenz, W. Steinert, and R. Zellner, in *Physical and Chemical Behaviors of Atmospheric Pollutants*, Comm. Eur. Communities, [Rep], pp. 192–202, 1982.
- <sup>13</sup>J. J. Margitan and R. T. Watson, *J. Phys. Chem.* **86**, 3819 (1982).
- <sup>14</sup>M. J. Kurylo, K. D. Cornett, and J. L. Murphy, *J. Geophys. Res. B* **87**, 3081 (1982).
- <sup>15</sup>A. R. Ravishankara, F. L. Eisele, and P. H. Wine, *J. Phys. Chem.* **86**, 1854 (1982).
- <sup>16</sup>P. Devolder, M. Carlier, J. F. Pauwels, and L. R. Sochet, *Chem. Phys. Lett.* **111**, 94 (1984).
- <sup>17</sup>C. A. Simith, L. T. Molina, J. J. Lamb, and M. J. Molina, *Int. J. Chem. Kinet.* **16**, 41 (1984).
- <sup>18</sup>J. J. Lamb, M. Mozurkewich, and S. W. Benson, *J. Phys. Chem.* **88**, 6441 (1984).
- <sup>19</sup>G. S. Jolly, G. Paraskevopoulos, and D. L. Singleton, *Chem. Phys. Lett.* **117**, 132 (1985).
- <sup>20</sup>P. S. Connell and C. J. Howard, *Int. J. Chem. Kinet.* **17**, 17 (1985).
- <sup>21</sup>R. A. Stachnik, L. T. Molina, and M. J. Molina, *J. Phys. Chem.* **90**, 2777 (1986).
- <sup>22</sup>A. R. Bossard, G. Paraskevopoulos, and D. L. Singleton, *Chem. Phys. Lett.* **134**, 583 (1987).
- <sup>23</sup>D. L. Singleton, G. Paraskevopoulos, and R. S. Irwin, *J. Phys. Chem.* **95**, 694 (1991).
- <sup>24</sup>S. S. Brown, R. K. Talukdar, and A. R. Ravishankara, *J. Phys. Chem.* **103**, 3031 (1999).
- <sup>25</sup>J. J. Aloisio and J. S. Francisco, *J. Phys. Chem. A* **103**, 6049 (1999).
- <sup>26</sup>(a) A. D. Becke, *J. Chem. Phys.* **97**, 9173 (1992); (b) **96**, 2155 (1992); (c) **98**, 5648 (1993); (d) C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B* **37**, 785 (1988); (e) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, and M. J. Frisch, *J. Phys. Chem.* **98**, 11623 (1994).
- <sup>27</sup>W. Hehre, L. Radom, P. v. R. Schleyer, and J. A. Pople, *Ab initio Molecular Orbital Theory* (Wiley, New York, 1986).
- <sup>28</sup>C. Gonzalez and H. B. Schlegel, *J. Chem. Phys.* **90**, 2154 (1989).
- <sup>29</sup>A. M. Mebel, K. Morokuma, and M. C. Lin, *J. Chem. Phys.* **103**, 7414 (1995).
- <sup>30</sup>M. J. Frisch, G. W. Trucks, H. B. W. Schlegel, P. M. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, *GAUSSIAN 94*, Revision D.3 ed. (Pittsburgh, PA, 1995).
- <sup>31</sup>S. J. Klippenstein, A. F. Wagner, R. C. Dunbar, D. M. Wardlaw, and S. H. Robertson, *VARIFLEX Version 1.00*, July 16, 1999.
- <sup>32</sup>E. Wigner, *J. Chem. Phys.* **5**, 720 (1937); J. Horiuti, *Bull. Chem. Soc. Jpn.* **13**, 210 (1938); J. C. Keck, *Adv. Chem. Phys.* **13**, 85 (1967); W. H. Miller, *J. Chem. Phys.* **65**, 2216 (1976); B. C. Garrett and D. G. Truhlar, *J. Phys. Chem.* **83**, 200 (1979); D. M. Wardlaw, and R. A. Marcus, *J. Chem. Phys.* **83**, 3462 (1985); S. J. Klippenstein and R. A. Marcus, *ibid.* **87**, 3410 (1987).

- <sup>33</sup>D. G. Truhlar, B. C. Garrtett, and S. J. Klippenstein, *J. Phys. Chem.* **100**, 12771 (1996).
- <sup>34</sup>J. Troe, *J. Chem. Phys.* **66**, 4745 (1977); **66**, 4758 (1977).
- <sup>35</sup>V. P. Varshni, *Rev. Mod. Phys.* **29**, 664 (1957).
- <sup>36</sup>S. J. Klippenstein, L. R. Kundhar, A. H. Zewail, and R. A. Marcus, *J. Chem. Phys.* **89**, 4761 (1988).
- <sup>37</sup>D. M. Wardlaw and R. A. Marcus, *Chem. Phys. Lett.* **110**, 230 (1984); *J. Phys. Chem.* **90**, 5383 (1986); *Adv. Chem. Phys.* **70**, 231 (1988).
- <sup>38</sup>A. F. Wagner, L. B. Harding, S. J. Robertson, and D. M. Wardlaw, *Springer Ser. Chem. Phys.* **61**, 203 (1996).
- <sup>39</sup>M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, *JANAF Thermochemical Tables*, 3rd ed. [*J. Phys. Chem. Ref. Data* **14**, (Suppl. 1), 1 (1985)].
- <sup>40</sup>K. Glänzer and J. Troe, *Ber. Bunsenges. Phys. Chem.* **78**, 71 (1974).
- <sup>41</sup>S. S. Brown, J. B. Burkholder, R. K. Talukdar, A. R. Ravishankara, R. Bianco, and J. C. Hynes, 16th International Symposium on Gas Kinetics, University of Cambridge, England, 23–27 July 2000, (unpublished), abstract No. PB3.
- <sup>42</sup>R. T. Skodje, D. G. Truhlar, and B. C. Garrett, *J. Phys. Chem.* **85**, 3019 (1981); T. C. Allison and D. G. Truhlar, in *Modern Methods for Multidimensional Dynamics Computations in Chemistry*, edited by D. L. Thompson (World Scientific, Singapore, 1998), p. 618.