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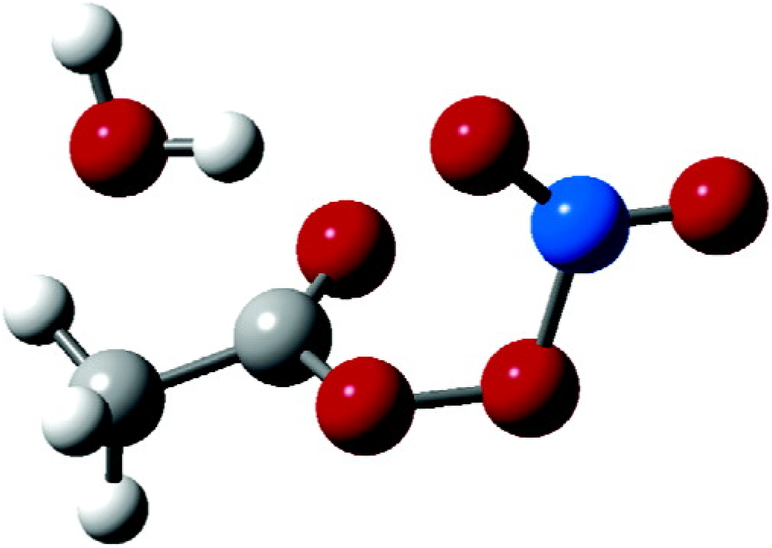

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An ab Initio Molecular Orbital Study of the Mechanism for the Gas-Phase Water-Mediated Decomposition and the Formation of Hydrates of Peroxyacetyl Nitrate (PAN)

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Abstract: There is uncertainty in the mechanism for the hydrolysis of peroxyacetyl nitrate (PAN), and experimental attempts to detect products of the direct reaction have been unsuccessful. Ab initio calculations are used to examine the energetics of water-mediated decomposition of gas-phase PAN into acetic acid and peroxynitric acid. On the basis of ab initio calculations, an alternative reaction mechanism for the decomposition of PAN is proposed. The calculations indicate that the barrier for one water addition to PAN is large. However, including additional water molecules reveals a substantially lower energy route. The calculations suggest that the formation of PAN hydrate complexes are energetically favorable and stable. Additional waters are increasingly efficient at stabilizing hydrated PAN.

Persistent differences exist between atmospheric models and observed field measurement of the abundances of nitrogen species in the chemistry of the troposphere.[1,2] The NO_x nitrogen budget ($NO_x = NO + NO_2$) to NO_y nitrogen budget ($NO_y = NO + NO_2 + HONO_2 + HOONO_2 + HONO + N_2O_5 +$ organic nitrates + peroxy nitrates) ratios are substantially larger from models than from the measured ones. The NO_x species are important in ozone destruction processes, which indirectly influences OH abundances in the troposphere.[3] To explain the discrepancies in the NO_x/NO_y ratios, removal processes of NO_y species has been suggested to be key,[4,5] in particular, processes that convert the major nitrogen reservoir species in the NO_y group to active nitrogen.[6] The major NO_y reservoir species are $HONO_2$, $HOONO_2$, and PAN. Peroxyacetyl nitrate (PAN), $CH_3C(O)OONO_2$, is a reservoir of both odd nitrogen and organic peroxy species in the atmosphere.[7−10] The oxidation of organics are precursors to the formation of PAN compounds, as they form acetyl peroxy radicals which then react with NO_2 to produce PAN. To explain the imbalance in NO_x/NO_y ratios, attention has been directed primarily to the hydrolysis of PAN and the heterogeneous loss of PAN. For PAN, there is confusion about how PAN is hydrolyzed in aqueous media. Roberts[13] proposed that PAN in water behaves similar to PAN in the gas phase in its initial decomposition, which is by homolytically breaking the NO bond to produce acetyl peroxy and the NO_2 radical via

$$CH_3C(O)OONO_2(PAN) \rightarrow CH_3C(O)O_2 + NO_2 \quad (1)$$

$$2NO_2 + H_2O \rightarrow HONO + NO_3^- + H^+ \quad (2)$$

$$2HONO \rightarrow NO + NO_2 + H_2O \quad (3)$$

Kames et al.[14] suggested that hydrolysis of PAN proceeded by a different mechanism than Roberts.[13] The hydrolysis of PAN as suggested by Kames et al.[14] produced acetic acid and $HOONO_2$ (PNA) by the addition of water via

$$CH_3C(O)OONO_2(PAN) + H_2O \rightarrow CH_3C(O)OH + HOONO_2 \quad (4)$$

$$HOONO_2 + H_2O \rightarrow H_2O_2 + HONO_2 \quad (5)$$

On the basis of the data, Kames et al.[14] were able to discount the mechanism of Roberts[13] but could not quantitatively support their own. One difficulty with the Kames et al.[14] mechanism has been the lack of verification of the products of the hydrolysis reaction despite unsuccessful experimental attempts. In the

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Table 1. Relative Energetics[a] for PAN + Water Reaction

nH_2O	method[b]	PAN + nH_2O	$(PAN\cdot nH_2O)_{complex}$	$(PAN\cdot nH_2O)_{TS}$	$\Delta E_{TS-complex}$
1	MP2/6-311+G(d,p)	0.0	−4.9	42.4	47.3
	MP4/6-311+G(d,p)	0.0	−5.1	41.6	46.7
	CCSD(T)/6-311+G(d,p)	0.0	−5.8	42.6	48.4
2	MP2/6-311+G(d,p)	0.0	−13.6	28.2	41.8
	MP4/6-311+G(d,p)	0.0	−13.8	28.0	41.8
	CCSD(T)/6-311+G(d,p)	0.0	−13.6	27.7	41.3
3	MP2/6-311+G(d,p)	0.0	−26.0	12.1	38.1
	MP4/6-311+G(d,p)	0.0	−26.6	11.4	38.0
	CCSD(T)/6-311+G(d,p)	0.0	−25.6	11.4	37.0

[a] In units of kcal mol^{-1}. [b] Relative energies were calculated for the various methods using geometries calculated at the MP2/6-311+G(d,p) level of theory.

present communication, we report results obtained using ab initio methods for the hydrolysis of PAN in the gas phase. We report the transition state and energetics for PAN with multiple waters and examine how these waters influence the gas-phase hydrolysis process.

All the geometries of the reactants, intermediates, and transition states were optimized using the second-order Moller−Plesset perturbation (MP2) method with the 6-31G(d,p) and 6-311+G(d,p) basis sets.[15] The transition states were evaluated to ensure they connected to the correct reactants and products using the intrinsic reaction coordinate (IRC) method. Vibrational frequency calculations using analytical second derivative method were also performed at MP2/6-31G(d,p) and MP2/6-311+G(d,p) levels of theory to verify if the transition states were first-order saddle points and the minimum energy structures were global minima. Calculations from the gas-phase homolytic decomposition pathways in PAN study of Miller et al.[16] suggest that MP2 optimized geometries can be used with single-point energy calculations to obtain reasonable relative energetics for PAN. In this study, the energies were calculated at the MP4SDTQ and CCSD(T) levels of theory with the 6-311+G(d,p) basis set using the geometry calculated at the MP2/6-311+G(d,p) level of theory. The relative energies of species of the reaction were included in Table 1. An important result that emerges from the data in Table 1 is the consistency between MP2, MP4, and CCSD(T) energetics suggesting that the results at the MP2 level are reasonable.

The structure of PAN is shown in Figure 1a for comparison with the transition states and complexes. As shown in Figure 1b, the transition state for the PAN + $H_2O \rightarrow CH_3C(O)OH$ + $HOONO_2$ reaction is four-centered. Relative to the isolated reactants (PAN + H_2O), the activation barrier is 42.6 kcal mol^{-1} at the CCSD(T)/6-311+G(d,p)//MP2/6-311+G(d,p) level of theory. Compared to the energetics for breaking the N−O bond in PAN through thermolysis,[16] the bond energetics is 30.7 kcal mol^{-1}. Consequently, the one water addition would not be competitive with the gas-phase homolysis of PAN. However, when the second water is brought into the system, this picture significantly changes.

The addition of a second H_2O into the PAN + H_2O reaction leads to several transition states which lead to acetic acid and $HOONO_2$. The lowest energy transition state shown in Figure 1d is a six-centered cyclic transition state, and as one can see from Figure 1b, it is quite different from the four-center transition state with one water. The activation energy barrier drops by 14.9 kcal mol^{-1} from that of the transition state with one water at CCSD(T)/6-311+G(d,p)//MP2/6-311+G(d,p) level of theory. The gas-phase activation barrier predicts that an additional water is effective in lowering the barrier. When the third water molecule is included to the PAN hydrolysis reaction, the trend to decrease the reaction barrier continues. The energy barrier between the eight-member-ring transition state and the isolated reactants (PAN and three water molecules) is 11.4 kcal/mol at CCSD(T)/6-311+G(d,p)//MP2/6-311+G(d,p) level of theory. This indicated that the PAN hydrolysis becomes more favorable with including more water molecules in the reaction. Consistently, the energy differences between the transition states and the corresponding reactant complexes (PAN + nH_2O) decrease with the increase in the number of water molecules involved in the reaction. These results also closely parallel those obtained for the hydrolysis of SO_3 where it was shown that while the direct reaction of SO_3 with water involved a four-center transition state and is quite energetically unfavorable,[17] an additional H_2O molecule provides a lower energy pathway for hydrolysis through the formation of a six-centered transition state.

The reaction barrier for the hydrolysis with two waters is 27.7 kcal mol^{-1} and with three waters is 11.4 kcal mol^{-1} above the free reactants at CCSD(T)/6-311+G(d,p)//MP2/6-311+G(d,p) level of theory. This is below the energetics (30.7 kcal mol^{-1}) required for homolytically breaking the NO bond. This is also below the energetics for breaking the O−O bond in PAN of 37.6 kcal mol^{-1} to give $CH_3C(O)O$ + NO_3. Therefore, reaction of PAN with water may be the important first step in the hydrolysis of PAN mechanism. We also find that the reaction is assisted by the addition of water. While the barrier for reaction of PAN with one water is large, an additional water is found to interact with PAN in a stabilizing fashion, and it provides a lower energy pathway for the formation of acetic acid and peroxynitric acid. The water in the reaction involving PAN + $2H_2O$ is similar to water dimer and PAN (see Figure 1d), and the transition state is reachable from starting with water dimer and PAN. This is very similar to the reaction of water dimer with SO_3 to catalyze the formation of sulfuric acid (H_2SO_4) that Morokuma[17] found.

In the course of the reaction of PAN with water, complexes are formed. In the 1:1 (PAN)(H_2O) complex, shown in Figure 1c, the water is oriented in the four-center configuration prior to moving into the transition state. The 1:1 (PAN)(H_2O) complex is 5.8 kcal mol^{-1} below the free reactants at CCSD(T)/6-311+G(d,p)//MP2/6-311+G(d,p) level of theory. The addition of the second water produces a 1:2 (PAN)(H_2O) complex that is structurally different from the 1:1 (PAN)(H_2O) complex but also significantly different from the six-center transition state in Figure 1e for the PAN + $2H_2O$ reaction. Interestingly, the 1:2 (PAN)(H_2O) complex is stable by 13.6 kcal mol^{-1} and the 1:3 (PAN)(H_2O) complex is stable by 25.6 kcal mol^{-1} relative to those of the isolated reactants at CCSD(T)/6-311+G(d,p)//MP2/6-311+G(d,p) level of theory. The formation of the hydrate complexes are barrierless processes. It is also clear from the energetics that water molecules added to the $PAN\cdot nH_2O$ complex are increasingly efficient at stabilizing the complex.

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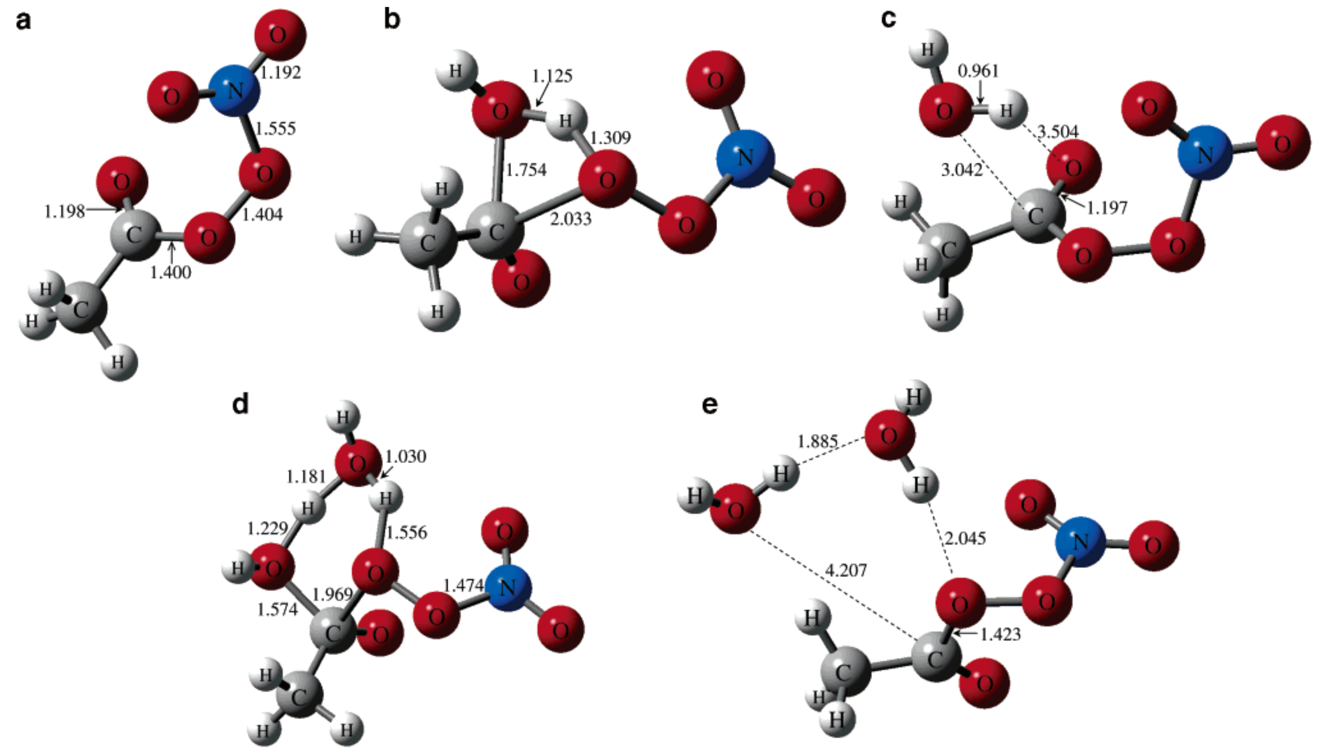

Figure 1. Optimized geometries, in Angstroms and degrees, at the MP2/6-311+G(d,p) level of theory for (a) PAN, (b) the transition state for PAN + H_2O → $CH_3O(O)OH$ + $HOONO_2$, (c) PAN·H_2O complex, (d) the transition state for PAN + $2H_2O$ → $CH_3C(O)OH$ + $HOONO_2$ + H_2O, (3) PAN·$2H_2O$ complex, and (e) PAN·$2H_2O$ complex.

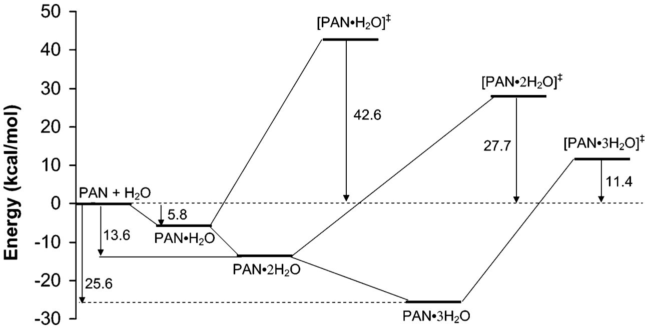

Figure 2. Summary of the potential energy surface for PAN + nH_2O. Results from the CCSD(T)/6-311G(d,p)//MP2/6-311+G(d,p) level of theory are included.

Given the strong binding of water to PAN, PAN−hydrates might be experimentally isolatable. These results also indicate that hydrates of PAN may form and persist under temperatures and water partial pressure conditions typical of the lower troposphere. The formation of PAN hydrates may help explain discrepancies between measured and modeled values of gas-phase PAN. Moreover, the strong association between PAN and water suggests that PAN may be accommodated on water surfaces, and these interactions may play a role in further promoting the formation of acetic acid and peroxynitric acid through hydrolysis in the aqueous phase.

Heterogeneous loss processes are well-known to be important in atmospheric chemistry, for instance, on surfaces of water, acid aerosol particles, or ice surfaces.[18] In the specific case of PAN, it is difficult to make a direct connection to the actual heterogeneous process. Nevertheless, the present calculation does indicate that there is an alternative pathway for PAN decomposition that is available in the presence of water, which is different from a homolysis route. When examining relative energies for key stationary points on the potential energy surface for the addition of multiple waters to PAN, as shown in Figure 2, a new picture of the reaction mechanism for the decomposition of PAN influenced by water emerges. The mechanism can be described by the following reaction sequence:

$$\mathrm{PAN} + \mathrm{H_2O} \rightleftarrows \mathrm{PAN{\cdot}H_2O} \tag{6}$$

$$\mathrm{PAN{\cdot}H_2O} + n\mathrm{H_2O} \rightleftarrows \mathrm{PAN{\cdot}}(n+1)\mathrm{H_2O} \tag{7}$$

$$\mathrm{PAN{\cdot}}(n+1)\mathrm{H_2O} \rightarrow \mathrm{CH_3C(O)OH} + \mathrm{HOONO_2} + (n-1)\mathrm{H_2O} \tag{8}$$

These calculations demonstrate that water plays an important role in promoting PAN decomposition and in the formation of PAN hydrates.

Supporting Information Available: Complete ref 15. This material is available free of charge via the Internet at http://pubs.acs.org.

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