

Phosphoric Acid – Methylamine Proton Transfer

1. Introduction:

Proton transfer in hydrogen bonded systems plays an essential role in a diverse range of devices and physical phenomenon, from electrochemical fuel cells [1] to signal transmission in biological systems [2]. The process of transferring a proton H^+ intermolecularly involves bond breaking, bond forming, and the accompanying redistribution of electron density. Although it is of great importance to many fields, the underlying mechanisms responsible for intermolecular proton transfer are not possible to generalize since the process is species dependent.

Liquid phosphoric acid has the highest proton conductivity measured to-date, and therefore it is interesting candidate of study from a fundamental perspective [3]. Likewise, its role in applied settings e.g. metabolism and proton-exchange membrane fuel cells, are as important of roles as any other proton-transferring species. This study focuses narrowly on the interaction between a phosphoric acid molecule (H_3PO_4 , $pK_{a1} = 2.16$) and a methylamine molecule (CH_3NH_2 , $pK_b = 3.38$). Methylamine is an interesting candidate due to its similar-but-opposite pK value, suggesting the proton transfer in the following reaction might be close to isoenergetic.



Phosphoric acid (PA) consists of a central phosphorus atom double-bonded to an oxygen atom and three hydrogenated oxygen atoms which share three-fold rotational symmetry (Fig 1.). Methylamine (MA) on the other hand has two-fold planar symmetry and consists of a methyl group bonded to an amino group.

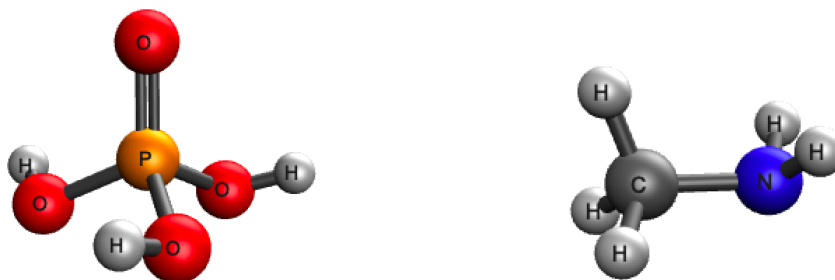
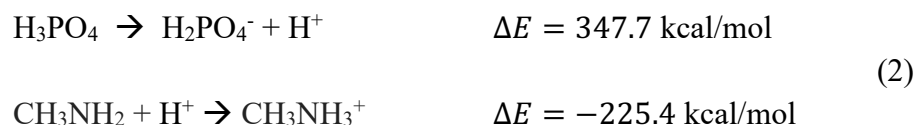


Figure 1: (left) Phosphoric acid and (right) methylamine molecules in their neutral form.

In order to estimate the spontaneity of proton shuttling between the molecules in reaction (1), the gas-phase proton-loss and proton-gain energies for PA and MA, respectively, were calculated as follows (methods specified in section 2).



Thus, PA's affinity to hold its proton is stronger than MA's affinity to acquire a proton, indicating that reaction (1) is unlikely to be spontaneous. However, the nature of the barrier is unknown. It is the aim of this study to locate the PA-MA intermolecular proton-transfer transition state, map the potential energy barrier, and to test a single water molecule's ability to act as a catalyst in changing the barrier's shape and height.

2. Methods:

All ab initio calculations were carried out on the Q-Chem 5.2 set of programs using the B-LYP exchange correlation hybrid functional and a basis set of double-zeta-quality, cc-pVDZ. This procedure was selected after careful review of computational studies in the literature involving small clusters of PA [1, 3], MA [2, 4], and water [5]. In particular, it was found this procedure out-performed Hartree-Fock theory and density-functional theory in efficiently finding global minima in the potential energy landscape of PA clusters (n=1- 4) [1]. Furthermore, a comprehensive comparison of dozens of theoretical methods applied to water clusters (n=1- 6) determined that the B-LYP hybrid functional with a basis set of double-zeta quality performed closest to the more computationally- expensive, gold standard MP2 theory [5].

The proton-loss and proton-gain energies in reaction (2) were obtained by running Q-Chem geometric optimization jobs for the charged H_2PO_4^- and CH_3NH_3^+ molecules as well as the neutrals H_3PO_4 and CH_3NH_2 . The energy difference between products and reactants of the isolated, optimized molecules are the values show in (2).

For the interaction between PA and MA, the initial geometry was first optimized to the minimum-energy configuration shown in Figure 2 below. A constrained potential energy scan (PES) was then performed in Q-Chem to force the PA's O-H separation from 0.8 to 2.4 Å in increments of 0.5 Å. At each step in the scan, the other atoms were allowed to relax to their energetic minima around the constrained O-H separation. Similarly, the PA-MA-H₂O structure was optimized in three configurations, then fed into an O-H stretching PES. An MMFF94 molecular mechanics force field was used to narrow all possible orientations to the three local min shown in Figure 3. The three geometries correspond the MA bonded to a fixed OH group ($\{\text{O,H}\}=\{7,8\}$ in figure 3), with the water then placed at each three OH groups— configuration 1 $\{\text{O,H}\}=\{5,6\}$, configuration 2 $\{\text{O,H}\}=\{1,4\}$, and lastly configuration 3 $\{\text{O,H}\}=\{7,8\}$ with the water between the MA and PA. Possible transitions states (TS) were located on the resulting PES scans, marked by arrows in Figures 2 and 3. To map reaction paths, the configuration at each of

these marked points was fed into a Q-Chem frequency job, followed by a transition state job, a frequency job, and lastly a reaction path job. Wherein reaction path jobs failed, well depths were measured by the difference between the well's energy (measured by an optimization job starting from transition state), and the energy of the barrier (measured by a transition state job).

To estimate the frequency of the PA-MA proton transfer from well 1 to well 2 across a range of temperatures, transition state theory was employed according to Eq. 1.

$$k(T) = \frac{k_B T}{h} \frac{Q^\pm}{Q_{MA} Q_{PA}} e^{-E_o/k_B T} \quad \text{Eq. 1}$$

where the molecular partition function Q is the product of translation, rotation, and vibrational partition functions $Q = Q_T Q_R Q_V$, the transition state partition function Q^\pm is the same but excluding the Q_T contribution, E_o is ZPE-corrected well 1 depth as per ab initio calculations, and h is Planck's constant. The individual partition functions were calculated as per their standard definitions below in Eq. 2 where μ is the PA-MA reduced mass and σ is the symmetry factor (= 1 for PA-MA TS, = 1 for MA, = 3 for PA). The frequencies and moments of inertia were obtained from Q-Chem frequency jobs.

$$Q_T = \left(\frac{2\pi\mu k_B T}{h^2} \right)^{3/2} \quad Q_R = \frac{\sqrt{\pi}}{\sigma} \left(\frac{8\pi^2 k_B T}{h^2} \right)^{3/2} (I_A I_B I_C)^{1/2} \quad Q_V = \prod_i^N \frac{1}{1 - e^{-h\nu_i}} \quad \text{Eq. 2}$$

Table 1: Molecular moments of inertia, calculated via frequency jobs on Q-Chem.

	I_A ($amu \cdot Bohr^2$)	I_B ($amu \cdot Bohr^2$)	I_C ($amu \cdot Bohr^2$)
PA-MA TS	464.93986	1590.4451	1639.96326
MA	22.58941	89.96951	91.37336
PA	397.30115	405.07325	405.07344

3. Results and Discussion:

The global minimum energy configuration for MA-PA has three-fold rotational degeneracy due to the symmetry equivalence of the three OH groups. The bonding OH group in Fig 2. was stretched in a PES scan resulting in a double-well potential with a mid-point barrier height of ~ 3.43 kcal/mol. Indeed, the proton transfer reaction (1) was found to be energetically uphill as suggested by the ΔE values in reactions (2). The mid-point of the barrier corresponds to a transition state wherein proton transfers to form NH_3 on the methylamine and the charged reactants of (1) are formed. As the O-H is stretched past 1.7 Å, the MA gives a proton back to PA. As seen in Figure 2, the NH_3 rotates to donate a different proton to the PA's double-bonded oxygen, and the energy of the system drops into the second well.

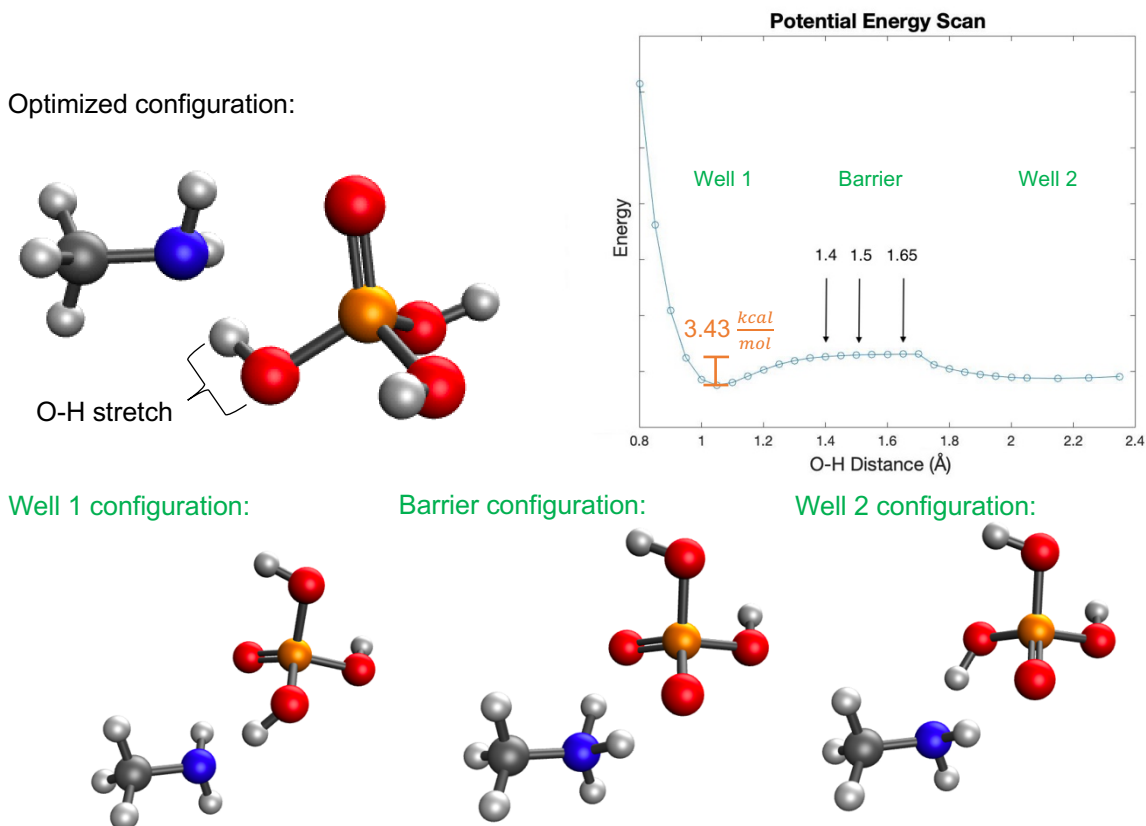


Figure 2: (top-left) Global minimum-energy configuration for PA-MA, degenerate with PA's three-fold rotation symmetry. (top-right) The O-H stretch PES scan. Arrows indicate the transition state point tested in rpath scans. (bottom) The corresponding configurations for points along the scan. Notice the MA pick up a proton, then donate a different proton back to the PA.

The PES barrier height is likely inaccurate since the forced O-H stretch is an artificial constraint and does not represent proton transfer's natural reaction path. To obtain the true barrier height of the proton transfer a Q-Chem reaction path job was performed. In a reaction path job, a transition state is specified at the onset and a path along the PE surface's saddle curve down to a local minimum is followed. Feeding the transition state near O-H = 1.65 Å configuration, the reaction path job traveled into well 2 and measured depth of 2.5809 kcal/mol, as shown in Fig. 3 right. No reaction path scans successfully navigated the MA-PA structure into well 1, however, well 1's depth was still able to be measured by taking the difference between the transition state and the optimized well 1 configuration. Figure 3 left shows an optimization job starting close to the transition state and moving into well 1's minimum, marking the bottom of well 1. The top of well 1 was taken as the transition state optimized structure, resulting in a well depth of -3.481 kcal/mol. Applying this method to well 2 yielded barrier height within 4% of the reaction-path-measured depth. Zero-point vibrational energies (ZPE) were found to be

69.096, 68.148, and 69.011 for well 1, the barrier, and well 2, respectively. The final ZPE-corrected wells depths are then -2.533 and -1.718 kcal/mol for wells 1 and 2, respectively.

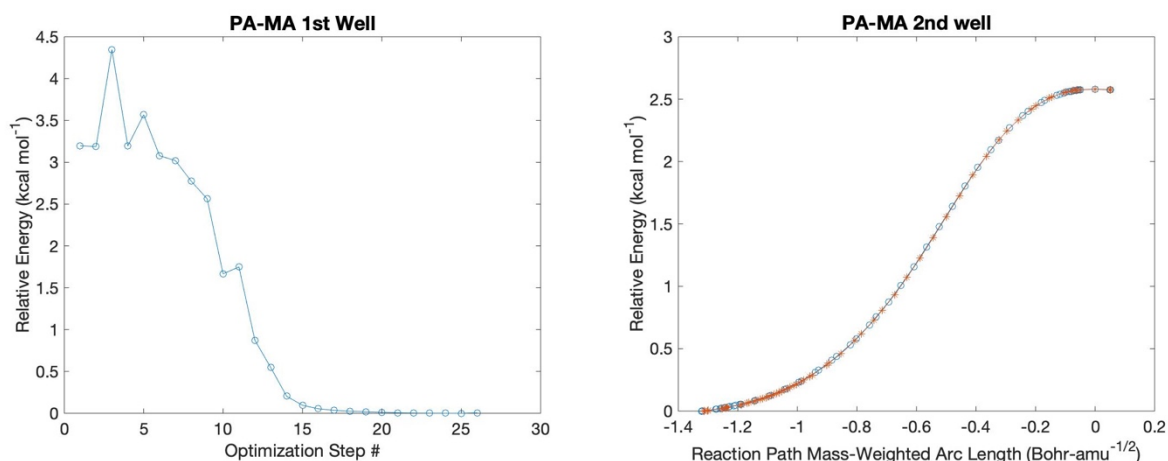
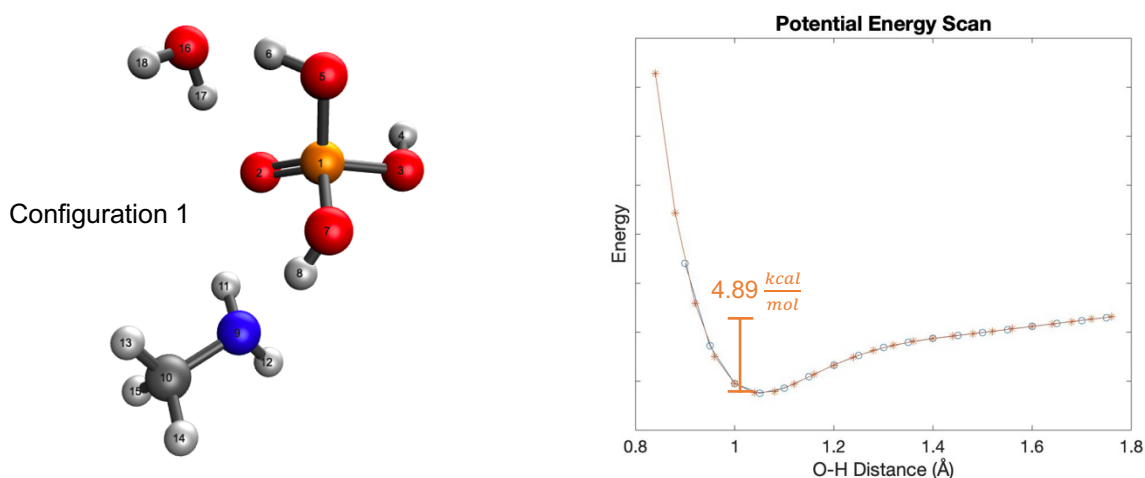


Figure 3: (left) Optimization job starting close to the transition state, used to measure the bottom of well 1 and (right) well 2's depth as determined by a reaction path job.

To determine a water molecule's ability to alter the height and shape of this double-well potential, similar methods were applied to a PA-MA-H₂O structure with three starting configurations corresponding to a H₂O-PA hydrogen bond at each of the PA's three OH groups. The PES in Figure 4 suggest different barrier shapes and heights for each of the three configurations— with double-well potentials for configurations 2 and 3, but not for configuration 1. In configuration 1, the MA failed to transfer a proton back to PA even at high O-H stretch lengths, due to the proximity of water's hydrogen (atom label = 18). Furthermore, in configuration 3, the H₂O acted as both the proton acceptor and donor. Thus, only configuration 2 resembled the reaction of the PA-MA system 'catalyzed' by H₂O.



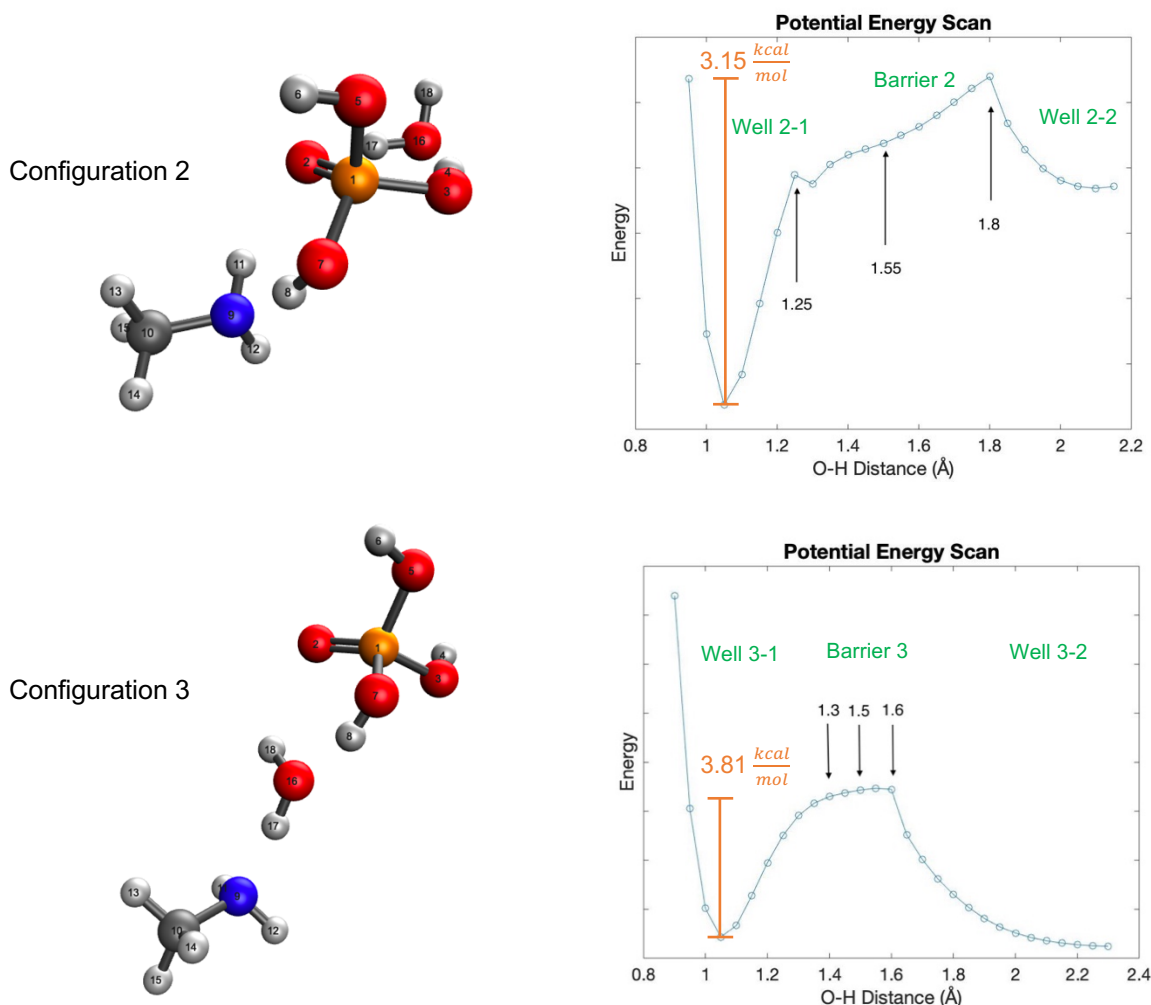


Figure 4: (left) Three initial configurations for PA-MA-H₂O PES scan and **(right)** the corresponding O-H stretch PES scan.

In order to more accurately measure the well depths for wells 2-1, 2-2, 3-1, and 3-2, reaction path jobs were run starting from transition state configurations. These efforts were successful for wells 2-1 and 2-3 but unsuccessful for wells 3-1 and 3-2. Wherein reaction path jobs failed to run the system to a certain well, well-depth is reported as the energy difference between the optimized transition state and well configurations, similar to PA-MA well 1. These results are summarized in Figure 5 and Table 2.

As previously discussed, the reaction of configuration 2 follows the PA-MA system wherein the first proton transfer is PA \rightarrow MA and the second is MA \rightarrow PA. It was found the addition of a single H₂O molecule decreases the barrier height and increases the asymmetry of the double well potential for this reaction (see Figure 5). In both the PA-MA and PA-MA-H₂O system, well 1 is deeper than well 2 due to the direction of PA's electropositive hydrogens (#4 and #6) favoring the placement of the third hydrogen (atom label 8) on oxygen 7 rather than

oxygen 2. This asymmetry is heightened in PA-MA-H₂O configuration 2 system because the water's hydrogens (#17 and #18) are also closer the #2 oxygen.

Table 2: Well depths for PA-MA-H₂O configurations 2 and 3, reported in kcal/mol.

Method:	2-1 depth	2-2 depth	3-1 depth	3-2 depth
Rpath	2.916	0.888	--	--
opt(ts) – opt(well)	3.202	1.086	3.815	3.976
ZPE -corrected Rpath	1.776	0.002	--	--
ZPE -corrected opt(ts) – opt(well)	2.062	0.200	2.903	3.306

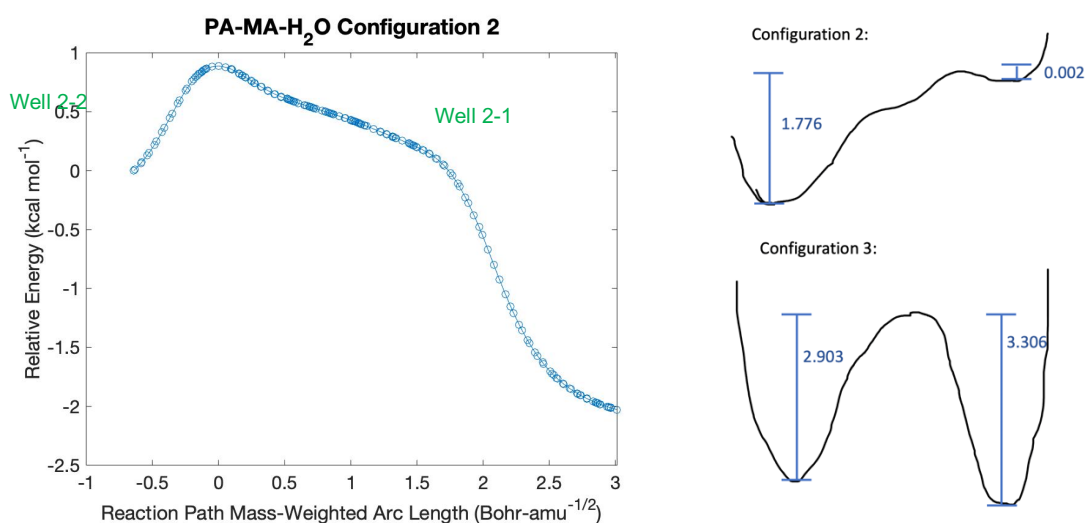


Figure 5: (left) Reaction-path scan for PA-MA-H₂O configuration 2. (right) graphical representation of the barriers based on ZPE- corrected well depth, reported in kcal/mol.

Since the proton transfer in configuration 3 occurs from PA → H₂O and back, it must be taken as a separate case from the PA → MA proton transfers. This proton transfer also followed a double-well potential, suggesting there likely is a generalized principal of forward and reverse proton transfer between PA and any proton-accepting species with additional hydrogens in close proximity to the PA's double-bonded oxygen. The ZPE-corrected well depths for 3-1 and 3-2 were found to be 2.903 and 3.306 kcal/mol, respectively. Given MA's status as a weak base, it is not surprising that the potential wells for the PA - H₂O proton transfer are deeper than PA - MA proton transfer. Surprisingly, however, the wells were only deeper by 1-2 kcal/mol, suggesting that the presence of MA significantly catalyzes the PA - H₂O proton transfer. Future studies could investigate the extent of this catalysis by studying PA- H₂O clusters.

The rate of the proton-transfer for PA-MA at room-temperature was found to be

$1.8494 \times 10^{-11} \text{ cm}^3/\text{molecule sec}$. The rate from 100 to 400 K is shown in Fig. 6 below.

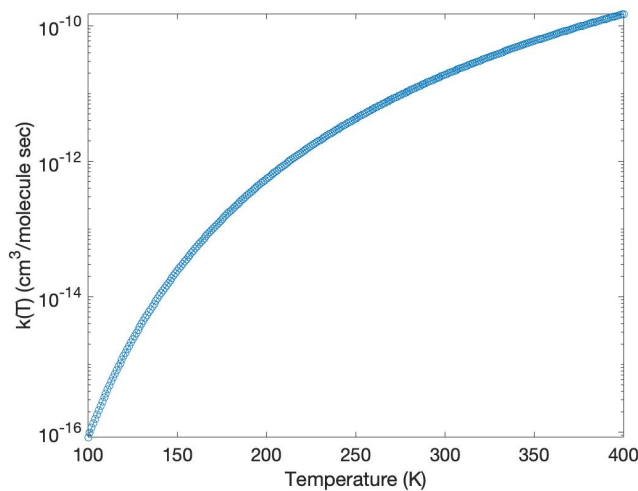


Figure 6: Rate constant $k(T)$ from 100 to 400 K.

4. Conclusions:

The PA-MA proton transfer has been determined to be energetically unfavorable, with a barrier of approximately 2 kcal/mol. Upon proton transferred, the system is at a transition state wherein it can give the same proton back or donate a separate proton to a separate OH group on the PA molecule. Therefore, the proton transfer exhibits a double-well potential for the two possibilities. The H₂O-PA behaves identically, but with greater well depths, indicating this double-well behavior is likely to be observed in all PA proton transfers wherein the proton acceptor has multiple hydrogens. The ZPE-corrected well depths for PA-MA, PA-MA- H₂O configuration 2, and PA-MA- H₂O configuration 3 have been found to be between 0.002 and 3.306 kcal/mol. Transition state theory predicts rate of the proton-transfer for PA-MA is approximately $1.8494 \times 10^{-11} \text{ cm}^3/\text{molecule sec}$ at room temperature.

5. References:

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