First principles computational study on hydrolysis of hazardous chemicals phosphorus trichloride and oxychloride (PCl3and POCl3) catalyzed by molecular water clusters

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Using first principles calculations we unveil fundamental mechanism of hydrolysis reactions of two hazardous chemicals PCl3and POCl3with explicit molecular water clusters nearby. It is found that the water molecules play a key role as a catalyst significantly lowing activation barrier of the hydrolysis via transferring its protons to reaction intermediates. Interestingly, torsional angle of the molecular complex at transition state is identified as a vital descriptor on the reaction rate. Analysis of charge distribution over the complex further reinforces the finding with atomic level correlation between the torsional angle and variation of the orbital hybridization state of phosphorus (P) in the complex. Electronic charge separation (or polarization) enhances thermodynamic stability of the activated complex and reduces the activation energy through hydrogen bonding network with water molecules nearby. Calculated potential energy surfaces (PES) for the hydrolysis of PCl3and POCl3depict their two contrastingly different profiles of double- and triple-depth wells, respectively. It is ascribed to the unique double-bonding O = P in thePOCl3. Our results on the activation free energy show well agreements with previous experimental data within 7 kcal mol^{-1} deviation.

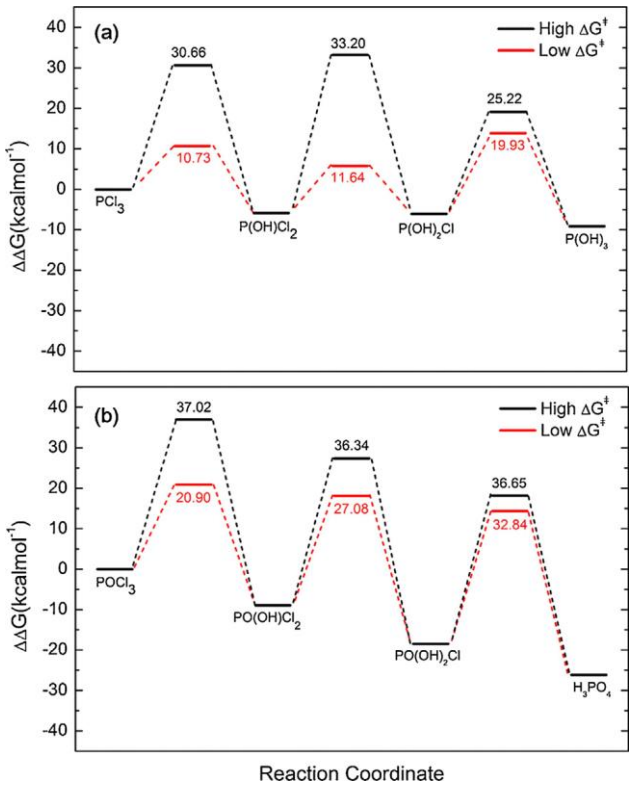

Figure 1. Calculated free energy diagrams of the hydrolysis of (a) $PCl_3$and (b) $POCl_3$ in a stepwise manner

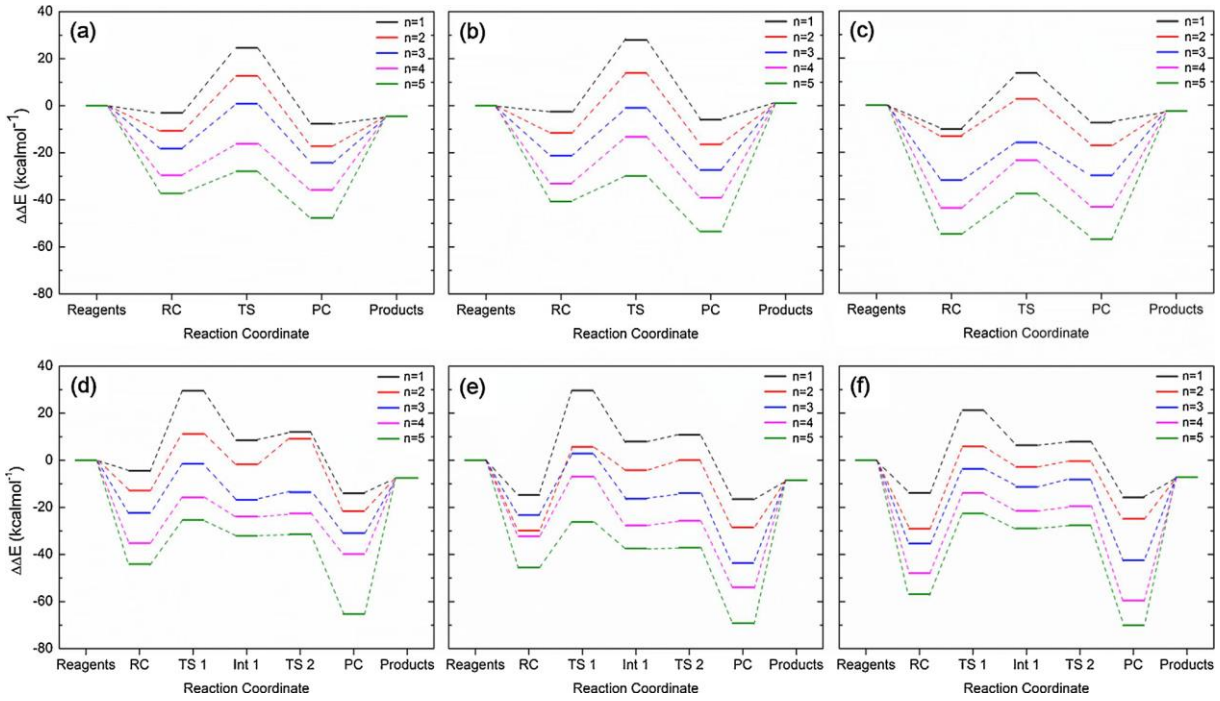

Figure 2. Potential energy surface (PES) for the hydrolysis of PCl_3 and $POCl_3$ and their intermediates with varying the number of adjacent water molecules (n): (a) PCl_3, (b)$P(OH)Cl_2$, (c) $P(OH)_2Cl$, (d) $POCl_3$, (e) $PO(OH)Cl_2$, (f) $PO(OH)_2Cl$.

Reference

1. H. Jung, J. Kang, H. Chun, B. C. Han, Journal of Hazardous Materials 341 (2018) 457–463