

제일원리 계산을 통한 유해화학물질 PCl_3 와 POCl_3 의 물분자 촉진 수화반응 연구
First Principles Study on Hydrolysis of Hazardous Chemicals PCl_3 and POCl_3 Catalyzed
by Water Molecules

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초 록: Using first principles calculations we unveil fundamental mechanism of hydrolysis reactions of two hazardous chemicals PCl_3 and POCl_3 with molecular water clusters nearby. It is found that the water molecules play a key role as a catalyst significantly lowering the activation barriers by transferring its protons to the reaction intermediates. Interestingly, torsional angles of molecular complexes at transition states are identified as a vital descriptor on the reaction rate. Analysis of charge distribution over the complexes further reinforces the finding with atomic level correlation between the torsional angle and variation of the orbital hybridization state of P in the complex. Electronic charge separation (or polarization) enhances thermodynamic stability of the activated complex at transition state and reduces the activation energy through hydrogen bonding network with water molecules nearby. Calculated potential energy surfaces (PES) for the hydrolysis reactions of PCl_3 and POCl_3 depict their two contrastingly different profiles of double- and triple- deep wells, respectively. It is ascribed to the unique double-bonding O=P in the POCl_3 . Our results on the activation free energy show well agreements with previous experimental data within 7kcalmol^{-1} deviation.