THREAT AGENT DEFEAT MODELING AND TESTING USING WMD SIMULANTS

Mechanistic Diversity And The Role Of Water In The Hydrolysis Of Sarin By Single Transition Metal Atoms On MoF-808

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Zr-based metal-organic frameworks (Zr-MOFs) are one of the most promising materials for the decomposition of chemical warfare nerve agents in solution. However, recent studies on the hydrolysis of gaseous nerve agents by Zr-MOFs indicate that catalytic activity is inhibited by the strong binding of the nerve-agent hydrolysis products to the catalytic active site on the MOF. Our recent works have shown that product inhibition can be ameliorated when the hydrolytic chemistry is driven by a single transition-metal atom deposited on the surface of the Zr-MOFs. Specifically, a detailed examination of the mechanisms of Sarin hydrolysis by Zn(II) and Ti(IV) single atoms on MOF-808 using high-accuracy electronic-structure methods shows a dramatic reduction in the rate-limiting product desorption step, unique conformer-dependent mechanisms, and novel, hitherto unreported hydrolysis products. In addition, current efforts are aimed at incorporating the hygroscopic character of Zr-MOFs into the simulation environment. Preliminary data suggests that the single-atom catalytic sites are saturated with water under operational conditions. This revelation brings into question the utility of previously developed gas-phase hydrolysis mechanisms and aggrandizes the role of water in the degradation of nerve agents with Zr-MOFs. Our results suggest that the microsolvated environment at the MOF surface under ambient conditions increases catalytic performance by further reducing the strength of the interaction between the hydrolysis products and the MOF. Our mechanistic studies leverage high-accuracy DLPNO-CCSD(T) calculations that serve to benchmark the performance of popular DFT methods for complex reaction mechanisms catalyzed by transition metals.

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