PROTECTION - SCIENCE AND TECHNOLOGY ADVANCES FOR CHEMICAL AND BIOLOGICAL PROTECTION

Dependence of VX NMR Chemical Shifts on MOF (UIO-66-NH2) Solid

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Metal Organic Framework (MOF) compounds have been studied as substrates for filtration or protection.1 Fabrics that incorporate MOFs are under study for protective garment materials. The MOF surface can interact in a number of ways with organophosphates and organophosphonates. VX has a central methylphosphonate reactive center, and the 31P chemical shift depends on surrounding solvent.2 Changes in the chemical shift can be studied with High Resolution Magic Angle Spinning (HRMAS) 31P Nuclear Magnetic Resonance (NMR) Spectroscopy. A JEOL ECS-400 NMR instrument with a Doty HRMAS probe was used for the studies. MOF fabric was made by Akita Innovations (fabric incorporated UIO-66-NH2, Lot UMLDEC29C) and supplied for the study by Teledyne/FLIR (COR Jennifer Poole). When neat liquid VX was deposited on a solid MOF material (UIO-66-NH2), two well-resolved, distinct NMR peaks were observed. The peaks had a changing pattern as the VX reacts. A literature publication reported effects of the MOF on proton chemical shifts.3 Signals from both nonpolar and more polar environments may be related to interaction of the VX with the Zr metal center or with polar and less polar solvation environments. Kinetic plots indicate that over time the amount of VX in each environment shifts as the VX reacts to form the phosphorus-containing product, ethyl methylphosphonate (EMPA). The chemical shifts may be useful in monitoring the mechanism of reactivity and the role of excess water in the reactivity. This information will help optimize the reaction conditions. This may improve the use of MOFs for protective applications by improving the rate at which compounds of interest are decontaminated.

References:

J. E. Mondloch, M. J. Katz, W. C. Isley III, P. Ghosh, P. Liao, W. Bury, G. W. Wagner, M. G. Hall, J. B. DeCoste, G. W. Peterson, R. Q. Snurr, C. J. Cramer, J. T. Hupp, and O. K. Farha, “Destruction of chemical warfare agents using metal–organic frameworks,” Nature Mat. 2015, 14, 512-516.

W. R. Creasy, D. J. McGarvey, and C. A. S. Brevett, “Speciation of VX in Aqueous Solutions,” J. Phys. Chem. C 2013, 117, 22677 -22682.

A. Nandy, A. C. Forse, V. J. Witherspoon, and J. A. Reimer, “NMR Spectroscopy Reveals Adsorbate Binding Sites in the Metal-Organic Framework UiO-66(Zr),” J. Phys. Chem. C 2018, 122, 15, 8295-8305.

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