The following article “Energetics and Dynamics of the Reactions of O(3P) with Dimethyl Methylphosphonate and Sarin” appeared in American Chemical Society, Journal of Physical Chemistry A, Vol. 113 (2009) and may be found at: http://pubs.acs.org/.

Abstract

Electronic structure and molecular dynamics calculations were performed on the reaction systems $O(^3P)$ + Sarin and $O(^3P)$ + dimethyl methylphosphonate (DMMP), a Sarin simulant. Transition state geometries, energies, and heats of reaction for the major reaction pathways were determined at several levels of theory, including AM1, B3LYP/6-311G+(d,p), and CBS-QB3. The major reaction pathways for both systems are similar and include H-atom abstraction, H-atom elimination, and methyl elimination, in rough order from low to high energy. The H-atom abstraction channels have fairly low barriers (~10 kcal mol^{-1}) and are close to thermoneutral, while the other channels have relatively high energy barriers (> 40 kcal mol^{-1}) and a wide range of reaction enthalpies. We have also found a two step pathway leading to methyl elimination through O-atom attack on the phosphorous atom for DMMP and Sarin. For Sarin, the two-step methyl elimination pathway is significantly lower in energy than the single-step pathway. We also present results of $O(^3P)$ + Sarin and $O(^3P)$ + DMMP reaction cross sections over a broad range of collision energies (2-10 km sec^{-1} collision velocities) obtained with the direct dynamics method using an AM1 semi-empirical potential. These excitation functions are intended as an approximate guide to future hyperthermal measurements, which to our knowledge have not yet examined either of these systems. The reaction barriers, reaction enthalpies, transition state structures, and excitation functions are generally similar for DMMP and Sarin, with some moderate differences for methyl elimination energetics, which indicates DMMP will likely be a good substitute for many Sarin in $O(^3P)$ chemical investigations.