

Ideal Gas Thermodynamic Functions of Organophosphorous Compounds from Density Functional Theory Calculations

O.N. Ryzhova^S and O.V. Dorofeeva^C

Department of Chemistry, Moscow State University, Moscow, Russia
olga.d@ru.net

Organophosphorus compounds can be difficult to purify and handle in air, and application of calorimetric methods for determining heat capacities and entropies are the most difficult when phosphorus is present in the molecule. This study uses computational chemistry to estimate thermodynamic functions of organophosphorus compounds. A standard statistical thermodynamic method was employed for the calculation of ideal gas entropies, heat capacities, and enthalpies of organophosphorus compounds. Contributions from translation, vibration, and external rotation were calculated using the rigid-rotor harmonic-oscillator approximation. Internal rotational contributions were calculated by direct summation over the energy levels, which were obtained by the diagonalization of the one-dimensional Hamiltonian with a fitted torsional potential. The required molecular constants (structural parameters, vibrational frequencies, and internal rotation potentials) were obtained at the B3LYP density functional theory level. The optimized geometry was utilized to perform a relaxed potential surface scan. In this potential scan, the appropriate torsion angle was varied in 10 degree increments from 0 to 360 degrees while all other structural parameters were optimized. The resulting potential functions were approximated by a sin-cosine Fourier series.

The thermodynamic functions of a large number of organic phosphorus(III) and phosphorus(V) compounds were calculated in this work. Standard entropies and heat capacities were used to estimate the group contribution values for these compounds.

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