Enthalpies of Formation of Organophosphorous Compounds Determined by Current Methods of Computational Quantum Chemistry

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The enthalpies of formation of organophosphorous compounds are often unknown or known with relatively large uncertainties. These compounds can be difficult to purify and handle in air, and an application of experimental methods for determining enthalpies of formation presents problems. The theoretical methods used in this work to estimate the enthalpies of formation were chosen according to the size of the molecule. For molecules with up to ten nonhydrogen atoms ($P(CH_3)_3$, $P(C_2H_5)_3$, $P(OCH_3)_3$, $P(CN)_3$, $[(CH_3)_2N]_2PCN$, $C_3H_7OPCl_2$, $C_6H_5PH_2$, $O=P(CH_3)_3$, $O=P(OCH_3)_3$, $O=P(CH_3)Cl_2$, *et al.*) the enthalpies of formation were calculated from atomization energies obtained by the highly accurate composite Gaussian-3X (G3X) method. The method of isodesmic reactions with electronic energies from B3LYP/6-311 G(3df,p)//B3LYP/6-31G(d,p) single point calculations was used for larger molecules ($P[(CH_3)_2CHO]_3$, $P(C_6H_5)_3$, $[(C_2H_5)_2N]_2PCl$, $O=P(C_6H_5)_3$, $O=P(OC_6H_5)_3$, *et al.*).

The reliability of the theory was tested for the molecules with the best experimental data. The level of agreement was good, taking into account large uncertainties in the experimental data. The enthalpies of formation of more than 50 organophosphorous compounds calculated at the G3X level of theory allowed us to obtain a consistent and accurate set of group increments for estimating enthalpies of formation by the group additivity method. The new groups include different types of bonds between phosphorous and C, O, N, S, F, and Cl atoms, and significantly extend the applicability of Benson's group additivity method.

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