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The ideal gas thermochemistry of inorganic and organic phosphorous compounds and their ions

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ABSTRACT

The thermochemistry of phosphorus compounds containing 3 nerve gases, 1 insecticide, 65 inorganic neutral species and their ions, and 48 organic neutral and ion species, were calculated with the DFT G3B3 composite method and reported (in the supplement) as 7 term NASA polynomials to be used for combustion simulation schemes. 49 of the species and ions are reported for the first time.

1. Introduction

The thermochemistry literature of phosphorous compounds is relatively scarce and many phosphorous compounds are not reported. In addition many of the phosphorous compounds are toxic and phosphorus was used to synthesize warfare nerve agents and insecticides.

The main phosphorus lethal gases are Sarin, Tabun, Soman and VX and the insecticides are Parathion Fenthion and many more. Parathion for example is forbidden for use in many countries because of its toxicity to humans.

The burning and destruction of chemical gas warfare and insecticides, provide decomposition species containing phosphorous which are also poisonous. The controlled elimination of the compounds as well as the need to find effective antidotes for those exposed to these compounds needs simulation of chemical processes and these require the knowledge of the compound thermochemistry.

Unfortunately the experimental thermochemical data are scarcely available for phosphorus inorganic species and almost nonexistent for organic species because of complex technical and health problems associated with such experiments. Therefore only computed values are available. The first inorganic phosphorus species were published in the JANAF (1960) [1], NASA (1963) [2] and Gurvich [3] databases. Before the 21st century most computed values were done by approximation such as in Lias et al. GIANT tables [4] and in many of Gurvich's data [3]. Presently *ab-initio* and DFT calculations are used.

In the 21st century we encounter five outstanding publications on phosphorous species: Haworth and Bacskay in 2002 using CCSD(T) calculations [5]; Dorofeeva and Moiseeva in 2006 using for trivalent phosphorus compounds, G3X and G3X(MP2) calculations [6] and Dorofeeva et al. [7] in 2007 for pentavalent phosphorus compounds; Baer, and coworkers in 2007 [8] an experimental study by threshold photoelectron coincidence spectroscopy that includes also cations; finally Glaude and coworkers in 2015 [9] by the MP2 = Full/6-31G(d,p) level of theory for organic compounds and also CBS-QB3, G4, W1U and CCSD(T)/CBS for inorganic compounds.

In this article, we have preferred to concentrate on decomposition compounds and ions of the main four nerve gases and insecticides. The ions were mostly neglected in previous computations but are important for simulation of combustion processes where they may be forming in flames. The phosphorus species calculated in this study and their ions are listed in Tables 1–3.

The aim of this study is to provide updated thermochemical data of phosphorous inorganic and simple organic compounds and their ions, in polynomial format for researchers doing simulations of combustion of these species.

2. Calculation of the species

The compounds listed in this study were computed, with a few exceptions, with the DFT composite method widely known as G3B3 (G3/B3LYP) which is actually a sequential series of calculations using B3LYP/6-31G(d), followed by QCISD(T,E4T)/6-31G(d), followed by MP4/6-31+G(d), followed by MP4/6-31G(2df,p) and finally MP2(Full)/gen. The data obtained by this procedure provided atomization energies at 0 K and enthalpies of formation at 0 and 298.15 K, all as explained and tested by Baboul et al. [10]. All the

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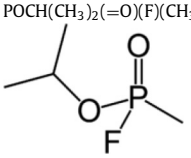
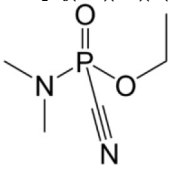
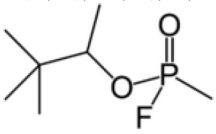
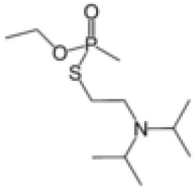
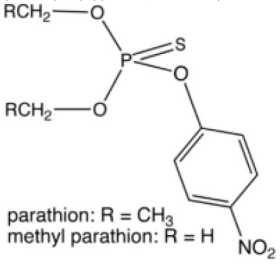
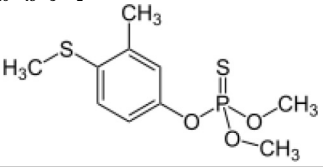
Table 1
Nerve gases and insecticides. Enthalpy of formation at 298 and 0 K, their uncertainties, the heat content C_p, entropy S and enthalpy increment $H_{298}-H_0$. The standard state corresponds to a pressure of 1 bar. Structure formulas from Wikipedia [42].

Compound	Mol. wt.	$\Delta_f H_{298}$ (kJ/mol)	$\Delta_f H_0$ (kJ/mol)	±kJ/mol	$C_{p\,298}$ (J/mol K)	S_{298} (J/mol K)	$H_{298}-H_0$ (kJ/mol)
$C_4H_{10}FO_2P$ SARIN $POCH(CH_3)_2(=O)(F)(CH_3)$ 	140.09437	−1005.834	−971.27	±20	159.442	411.754	30.443
$C_5H_{11}N_2O_2P$ Tabun $P\text{-}OC_2H_5(=O)(CN)(N(CH_3)_2)$ 	162.12688	−484.800	−446.291	±20	190.337	467.656	36.043
$C_7H_{16}FO_2P$ Soman* $CH_3C(CH_3)_2CH(CH_3)OP(=O)F(CH_3)$ 	182.17290	−1076.543	−982.971	±20	229.702	518.230	–
$C_{10}H_{26}NO_2PS$ VX* 	267.37	−746.34					
$C_8H_{10}NO_5PS$ Parathion* $(CH_3O)_2P(S)(\text{-}O\text{-}C_6H_4\text{-}NO_2)$ 	291.26	−760.15					
$C_{10}H_{15}O_3PS_2$ Fenthion 	278.33006	−688.77	−638.62	±20.	288.227	575.876	51.104

* The enthalpy of formation was calculated by GA [9].

calculations were performed with the Gaussian 03 set of programs [11].

The G3B3 method was used because as it will be shown in our calculations, G3B3 gives results at the same error level as other methods, compared to Dorofeeva and Moiseeva (G3X) [6], Glaude and coworkers (CBS-QB3, G4, W1U) [9], and to the results of Simmie and Sommers [12] compared to our database species [14]. The vibrations and moments of inertia were calculated at the B3LYP/6-31G(d) theory level as used by most methods and researchers [6,8,9,34], and as preferred for most species by the NIST CCCBDB database [13]. Also the G3B3 method was used because of its compatibility with our Thermochemical Database [14] which has the largest set of calculated results of G3B3 atomization enthalpies of formation.

It should be stated here that the G3B3 is very convenient in terms of calculation time, but it is restricted to molecules of ~8–10 heavy atoms and up to 12 heavy atoms for very symmetric molecules. In cases where these limitations were exceeded (i.e., the nerve gases in Table 1) only the vibrations and moments of inertia were calculated using B3LYP/6-31G(d) method, and the enthalpy of formation was taken from the literature cited.