Bond Dissociation Energies of Organophosphorus Compounds: an Assessment of Contemporary Ab Initio Procedures

Karen Hemelsoet,*,† Frederick Van Durme,†,¶ Veronique Van Speybroeck,*,†
Marie-Françoise Reyniers,‡ and Michel Waroquier†

Center for Molecular Modeling, Ghent University, Technologiepark 903, B-9052 Zwijnaarde, Belgium, QCMM-alliance, Ghent-Brussels, and Laboratory of Chemical Technology, Ghent University, Krijgslaan 281-S5, B-9000 Ghent, Belgium

E-mail: karen.hemelsoet@ugent.be; veronique.vanspeybroeck@ugent.be

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*To whom correspondence should be addressed

†Center for Molecular Modeling, Ghent University, Technologiepark 903, B-9052 Zwijnaarde, Belgium, QCMM-alliance, Ghent-Brussels

‡Laboratory of Chemical Technology, Ghent University, Krijgslaan 281-S5, B-9000 Ghent, Belgium

¶Present Address: Yara Sluiskil B. V., Industrieweg 10, 4540 AA Sluiskil, the Netherlands

Abstract

Thermodynamic properties of phosphorus-containing compounds were investigated using high-level ab initio computations. An extended set of contemporary density functional theory (DFT) procedures was assessed for their ability to accurately predict bond dissociation energies of a set of phosphoranyl radicals. The results of meta- and double-hybrids as well as more recent methods, in particular M05, M05-2X, M06 and M06-2X, were compared with benchmark G3(MP2)-RAD values. Standard heats of formation, entropies and heat capacities of a set of ten organophosphorus compounds were determined and the low-cost BMK functional was found to provide results consistent with available experimental data. In addition, bond dissociation enthalpies (BDEs) were computed using the BMK, M05-2X and SCS-ROMP2 procedure. The three methods give the same stability trend. The BDEs of the phosphorus(III) molecules were found to be lower than their phosphorus(V) counterparts. Overall the following ordering is found: BDE(P-OPh) $<$ BDE(P-CH_3) $<$ BDE(P-Ph) $<$ BDE(P-OCH_3).

Keywords: ab initio computations, organophosphorus radicals, bond dissociation enthalpies, coke-inhibiting additives, assessment

Introduction

Phosphorus-containing molecules are important in a broad variety of chemical processes, such as biological systems, the synthesis of industrial chemicals, decomposition of pesticides and insecticides,[1] catalytic applications (ligands for transition metals)[2] and flame retardation.[3,4] Our interest in phosphorus-containing species stems from the (experimental) observation that these molecules can be used as efficient coke-reducing additives within thermal cracking processes.[5,6] Unfortunately, the development of kinetic models for this industrially important process has been hampered by a lack of accurate thermochemical and kinetic data as experimental enthalpies of formation are often unknown or known with relatively large uncertainties. Computational results can hence offer a viable alternative.[7,8]

Currently, only a handful of papers reports on ab initio thermochemical properties of phosphorus-containing compounds. Bauschlicher computed the heats of formation of the PO_n and PO_nH , n=1-3 species using B3LYP/6-31G(2df,p) geometries and (R)CCSD(T)/CBS energies.[9] Haworth and Bacskay used the same high-level method for a set of 18 compounds (P-containing hydrides, oxides and hydroxides), and the G3, G3X and G3X2 methods were assessed. It was found that the latter two methods reproduce the benchmark heats of formation within ± 8 kJ mol^{-1}. Problems were noticed for molecules containing unusual, i.e., multiple or cyclic, P-P bonds, and attributed to the poor performance of MP4 in the prediction of the $(2df,p)$ correction.[10] In addition, Haworth et al. studied several reactions of importance in the H + OH recombination reaction which is catalyzed by oxidation products of PH_3.[11,12] The G3X method was found to be superior to G2 and G3 for the prediction of heats of formation.[11] Matus et al. calculated heats of formation of P_2H_x and $P_2H_x(CH_3)_y$ compounds at the sophisticated CCSD(T)/CBS and MP2/CBS level, respectively.[13]

The computation of accurate thermochemistry for species containing second-row elements is known to depend on the use of 'tight' *d* functions.[14–16] Dunning et al. developed the cc-pV(n+d)Z sets, which are able to describe core polarization and 'inner loop' valence correlation effects for the atoms aluminum through argon.[17] Most studies have focussed on sulfur-containing compounds,[18–20] however some also tackled this issue for phosphorus-containing species.[9,21,22] It was overall found that the use of high-exponent *d* functions is very important in the determination of accurate energetics, whereas the impact on structures, i.e., bond lengths and angles, is slight. The present paper uses a large basis set, without however the explicit inclusion of tight d functions, focussing on the assessment of the electronic structure method.

Dorofeeva et al. obtained theoretical enthalpies of formation for a large set of organophosphorus compounds and derived Benson's group additivity values (GAV).[23,24] This method may be used to estimate the enthalpies of formation of larger molecules for which sophisticated computations become unfeasible and time-consuming. In the same spirit the GAV method has been investigated in detail on a large set of hydrocarbons and hydrocarbon radicals by some of the authors[25,26] using the CBS-QB3 method. The test set of the organophosphorus(III) study applied by Dorofeeva et al. involves 55 compounds, and the G3X, G3X(MP2) and B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p) levels of theory were considered. The G3X method was found to reproduce well-established experimental results to an accuracy of ± 10 kJ mol^{-1}.[23] Large differences (up to 30 kJ mol^{-1}) between experimental and computational data were reported for $P(C_2H_5)_3$ and $P(n\text{-}C_4H_9)_3$, however, it was suggested that the experimental data should be remeasured. These authors performed a similar study for a set of 40 organophosphorus(V) compounds for which heats of formations were calculated using the G3X methodology and compared with available experimental data.[24] For the majority of the species, differences between theory and experiment range between 6 and 29 kJ/mol, which is acceptable taking into account the combination of experimental and theoretical errors. However for some compounds having a P=O bond, differences up to 40 - 100 kJ/mol are obtained, which might relate to experimental uncertainties or a decreased accuracy of the G3X theory for this particular type of molecules.

The accurate calculation of BDEs has recently received a lot of attention.[27–30] A study of Hodgson and Coote investigating the relative stabilities of phosphoranyl radicals $^{\bullet}P(CH_3)_3X$ and introducing a new measure of stability, i.e., the α-radical stabilization energy (α-RSE), is of special importance to the present article.[31] As opposed to the standard RSE definition, the α-RSE measures the stability of the radical with respect to $P(CH_3)_2X$ instead of to $H\text{-}P(CH_3)X$, i.e. assessing the stability of the radical on the basis of its susceptibility to α-scission of the methyl radical rather than its susceptibility to hydrogen abstraction. The investigated radicals $^{\bullet}P(CH_3)_3X$ assume an almost undisturbed trigonal-bipyramidal geometry, with the X-group occupying an axial position, and the unpaired electron distributed between a $3p_{\sigma}$-type orbital and the σ^* orbitals of the axial bonds. The influence of various substituents (X=CH_3, SCH_3, OCH_3, OH, CN, F, CF_3, Ph) was examined. It was found that strong σ-acceptors or substituents exhibiting a weak P-X bond result in the largest radical stabilities. Comparison between the alternative α-RSE and standard RSE definition gives opposing trends for the stability of P-radicals with respect to C-radicals. It was however emphasized that this is not an effect of intrinsic radical stability, but of the lower stability of the P-H versus C-H, P-C versus C-C, or P-P versus C-C bonds. The study provides a large set of high-level G3(MP2)-RAD data and will be used as a benchmark in the present work. A profound performance study of this method has however not yet been done for phosphorus-containing species and hence we compute heats of formation for a set of small organophosphorus molecules for which experimental data is available. The excellent performance of G3(MP2)-RAD for other open-shell species is earlier reported, in particular for carbon-[29,58,59] and nitrogen-centered radicals.[60]

Phosphorus-containing additives have been shown to be effective in inhibiting coking rates during thermal cracking processes.[5,6,32–37] It is believed that the additives provide a film to passivate the metal surface to prevent it from catalyzing the coke formation, however reactions between the additives and the coke surface are also present and are the subject of a next study. A recent experimental study using SEM- and EDX-techniques reports on the changed morphology, i.e., softer coke, and lower concentration of metals in the coke when organophosphorus molecules are added to the naphtha feed.[32] The effect of various additives during naphtha pyrolysis has been described and compared. Comparison between the additives (given in Figure 1) triethylphosphite (TEP), triphenylphosphite (TPP), benzyldiethylphosphite (BDP) and triphenylphosphine sulfide (TPPS), revealed that the phosphor-sulfur compound is the most effective.[6] The coke inhibiting effect of triphenylphosphine (TPPn), tri-o-tolylphosphine (TTP) and triphenylphosphine oxide (TPPO) was also investigated, and for these three molecules, a higher effectiveness of the TPPO molecule was reported.[32] This behavior might relate to the observation that in case of dissociation of the P=O bond, two passivating radicals are formed. Various factors, i.e., phosphorus-carbon or phosphorus-oxygen bond strength, size of the molecule, and stability of the metal-phosphorus complex formed on the surface, are overall expected to be important for the coke-inhibiting efficiency.[32]

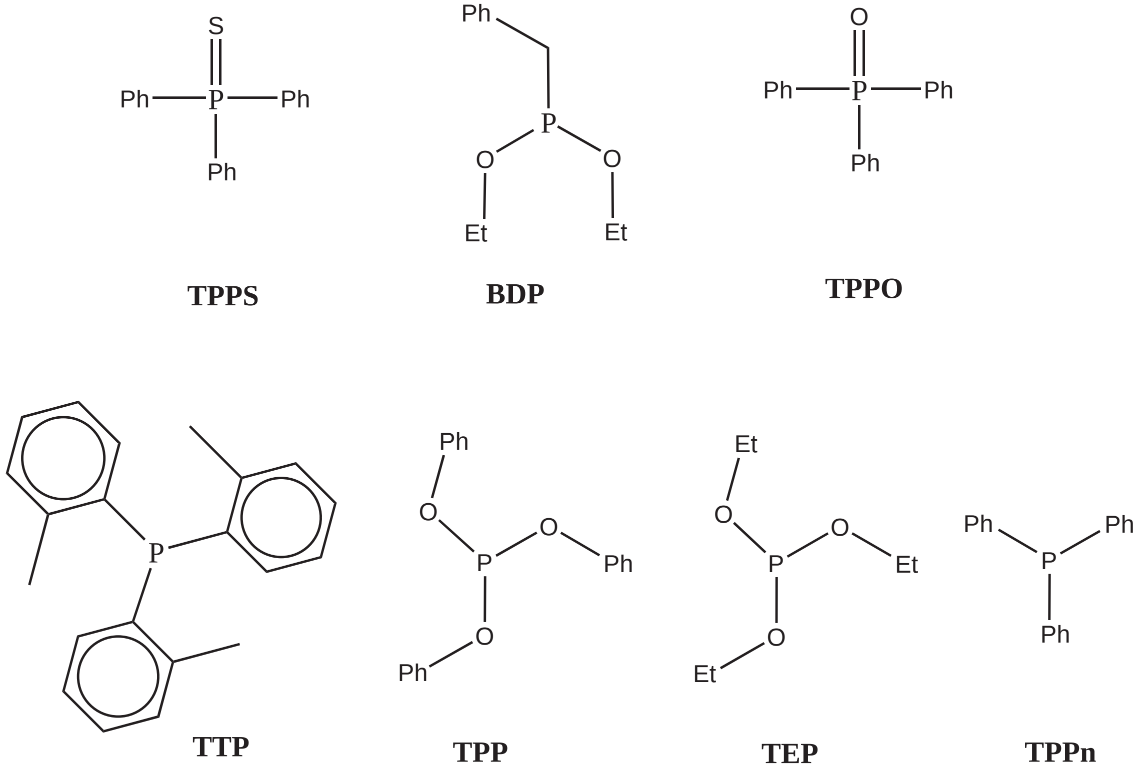


Figure 1: Representation of industrially applied phosphorus-containing additives, in order of decreasing efficiency for coke inhibition.[6,32]

This work represents a comprehensive ab initio study on P-containing species and has three primary aims. Firstly, we will assess a broad variety of current computational methods in order to determine an appropriate level of theory for the calculation of reliable bond dissociation properties of phosphorus compounds. Secondly, we will provide thermochemical data such as the enthalpy of formation, the heat capacity and the entropy for a set of phosphorus-containing species representing industrially important coke-inhibiting additives (Figure 1). This data can e.g. be used as input in microkinetic models. And thirdly, we will compute BDEs of these compounds to establish the stability of the formed radicals and their reactivity trends.

Computational Details

Standard ab initio molecular orbital theory and density functional theory calculations were carried out using the Gaussian03,[38] Molpro 2002.6[39] and NWChem5[40] software packages.

The bond dissociation energies D($^\bullet$P-C) and D($^\bullet$P-X) of the phosphoranyl radicals $^\bullet P(CH_3)_3X$ were calculated. These properties are defined as explained in the work of Hodgson and Coote,[31] using the reactions depicted in Figure 2. X_{ax} and X_{eq} refer to the axial and equatorial conformations, for which the axial conformation is the global minimum in all cases.

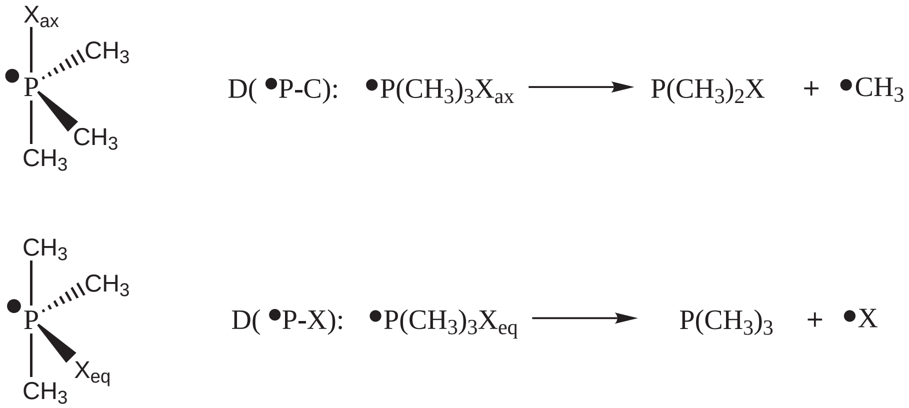


Figure 2: Investigated compounds and definition of bond dissociation energies as stated by Hodgson and Coote.[31]

Geometries were optimized at the B3LYP level of theory, in conjunction with the 6-31+G(d,p) basis set. Harmonic vibrational frequencies were computed at the same level of theory and were used to provide zero-point vibrational energies (ZPVEs) and to confirm the nature of the stationary points. We note that the level of geometry optimization is slightly different from that used in the original work of Hodgson and Coote,[31] where a 6-31G(d) basis set is applied. However, this has a negligible effect on the computation of bond dissociation energies. The ZPVEs were scaled using a factor of 0.9806.[41] Subsequent single-point energy calculations were performed using a variety of levels of theories. DFT-based hybrid and meta-hybrid methods, i.e., B3P86 (20% HF exchange),[42,43] B3LYP (20% HF exchange),[42,44] BMK (42% HF exchange),[45] MPW1K (42.8%

HF exchange)[46] and MPWB1K (44% HF exchange),[47] were investigated. A recent class of meta-hybrid GGAs involves the M05 (28% HF exchange),[48] M05-2X (56% HF exchange),[49] M06 (27% HF exchange)[50] and M06-2X (54% HF exchange)[49] functionals and was also tested. The M05-2X and M06-2X methods are recommended for calculating bond dissociation energies for systems that do not include metal atoms. The double-hybrid functionals B2PLYP (53% HF exchange and 27% MP2 correlation)[51] and MPW2PLYP (55% HF exchange and 25% MP2 correlation)[52] are also included in this assessment. These functionals have been introduced by Grimme and have been found to show promising performance in calculating thermochemical properties for the G3/05 test set.[52] Finally, MP2 and modified MP2 (SCS-MP2[53] and SOS-MP2[54]) methods were also tested for their performance. It was stated that SCS-MP2 clearly outperforms the B3LYP method albeit at similar computational costs.[53] This statement will be tested for the set of phosphorus-containing species. All single-point calculations were done in conjunction with the large 6-311+G(3df,2p) basis set. In addition to the cost-effective methods, the composite CBS-QB3 method was also assessed.[55,56] Calculations on radicals that were performed with a restricted-open-shell reference wave function are designated with an 'RO' prefix, opposed to the unrestricted-open-shell computations for which the 'U' prefix is omitted.

Using the results obtained in the level of theory section, bond dissociation enthalpies (BDEs) of a set of ten phosphorus-containing compounds, representing coke-inhibiting additives, were computed using B3LYP/6-31+G(d,p) geometries and BMK, M05-2X and SCS-ROMP2 energies in combination with the large 6-311+G(3df,2p) basis set. In addition, G3(MP2)-RAD results of some compounds are also computed. A scaling factor of 0.9989 was used for the thermal corrections to the enthalpy.[57]

Results and Discussion

Level of theory assessment

A set of phosphoranyl radicals as studied by Hodgson and Coote is used to investigate the influence of the level of theory on bond dissociation properties. The high-level G3(MP2)-RAD results reported in that work[31] are taken as benchmark values, although a profound performance study of this method has not yet been done for phosphorus-containing species. For other open-shell species, in particular carbon-[29,58,59] and nitrogen-[60] centered radicals, G3(MP2)-RAD performs excellent, but a sound basis for the difficult class of phosphorus-containing compounds is still missing. To remedy this limitation, we computed heats of formation for a set of small organophosphorus molecules for which experimental data is available. The G3(MP2)-RAD results, as well as CCSD(T)/CBS,[10] G3X and G3X2[11] values, are listed in Table 1.

Table 1: Heats of Formation at 298 K ($\Delta_f H^0_{298}$), in kJ/mol.

	G3(MP2)-RAD	CCSD(T)/CBS[10]	G3X (*G3X(RAD)*)[11]	G3X2[10]	Experiment
PH_2	129.9	131.8	134.7	128.9	108.8 ± 96.2[61] 138.5 ± 2.5[62]
PH_3	7.8	3.8	10.0	2.5	5.4 ± 1.7[61]
PO	-30.0	-31.8	-45.2 (*-32.2*)	-34.3	-23.4 ± 4.2[61] -28.5 ± 7.9[63] -27.9± 3.3[64]
PO_2	-281.2	-291.6	-289.5 (*-293.7*)	-292.5	-278.7 ± 10.9[63] -291.6 ± 10.0[64]
HPO	-90.7	-93.7	-92.0	-96.7	-56.9 ± 40.2[64]
HOPO	-455.1	-468.6	-461.5	-465.7	-462.8 ± 12.6[65]

The G3(MP2)-RAD, which aims to reproduce reliable estimates of the CCSD(T) energies in sufficiently large basis set, and computationally heavy CCSD(T)/CBS methods yield similar predictions for the heats of formation. Largest deviations exceeding 10 kJ/mol are noticed for PO_2 and HOPO but the predictions are still within the chemical accuracy. Both G3X and G3X2 (based on spin unrestricted calculations) perform equally well. The G3X method fails in reproducing the experimental heat of formation of the open-shell molecule PO, as already reported by Haworth and coworkers.[10] We note that our G3(MP2)-RAD results do not contain scalar relativistic corrections (ranging between -1.5 and -4.0 kJ/mol for the systems under investigations), as compared to reported CCSD(T)/CBS theoretical results.[9,10] Taking into account the sometimes large experimental uncertainties, in particular for PH_2 and HOPO, the present analysis shows that the G3(MP2)-RAD results agree with the available experimental data, a maximal deviation of 7.6 kJ/mol is obtained.

Returning to the set of larger phosphoranyl radicals,[31] a variety of low-cost levels of theory is assessed to identify a suitable procedure that might be applicable to larger systems. Computed bond dissociation energies (D($^\bullet$P-C) and D($^\bullet$P-X)), as defined in Figure 2, are tabulated in Table 2 and Table 3, respectively. The largest deviations (LD), mean deviations (MDs) and mean absolute deviations (MADs) from the G3(MP2)-RAD values are also listed. Compared to the original set, the substituents F and CF_3 are left out, as these are not relevant in case of coke formation during thermal cracking.

It is found that the generated G3(MP2)-RAD trend in terms of the substituents is maintained for all tested levels of theory, with exception of MPWB1K and CBS-QB3 in the case of breaking of the P-C bond. The first method interchanges the order of the D($^\bullet$P-C) values for the phenyl and methyl substituent. The CBS-QB3 method largely overestimates the D($^\bullet$P-C) value for the phenyl substituent (deviation of 48.0 kJ/mol). This composite method, and in particular the MP2 and MP4 contributions, suffer from large spin-contamination for all investigated phosphorus-containing radicals and we therefore would recommend the use of a restricted variant. In the present work, the CBS-QB3 method leads to substantial deviations from the G3(MP2)-RAD benchmark values (MD for D($^\bullet$P-C) and D($^\bullet$P-X) of 15.1 and 8.5 kJ/mol, respectively). This result is opposed to the conclusion reported by Menon et al. recommending CBS-QB3 (and other variations) for the accurate calculation of thermochemistry of carbon-centered radicals.[27] A general conclusion about the performance of the various methods in reproducing the benchmark values for both the D($^\bullet$P-C) and D($^\bullet$P-X) can not be drawn. Well performing methods in the prediction of D($^\bullet$P-C) generally

Table 2: Bond Dissociation Energies D($^\bullet$P-C), in kJ/mol. LD, MD and MAD, in kJ/mol, refer to the largest, mean and mean absolute deviation from the G3(MP2)-RAD values.

method X	C_6H_5	CH_3	CN	OH	OCH_3	SCH_3	LD	MD	MAD
B3P86	12.4	1.8	29.2	39.0	40.2	60.6	13.2	9.6	9.6
B3LYP	-7.6	-15.0	9.9	20.1	20.2	51.9	-12.7	-7.7	7.8
ROB3LYP	-7.1	-14.6	10.0	20.6	20.7	51.9	-12.2	-7.4	7.4
BMK	0.5	-7.8	17.3	24.8	25.8	53.1	-4.6	-2.0	2.9
ROBMK	0.7	-7.9	17.1	25.1	26.1	53.0	-4.4	-2.0	2.7
MPW1K	1.9	-5.4	21.2	29.9	30.3	51.2	5.2	0.6	1.8
MPWB1K	8.7	11.2	25.5	35.3	36.0	57.5	16.5	8.1	8.1
ROMPWB1K	7.9	-1.4	24.3	34.5	35.0	55.9	8.3	5.1	5.1
M05	3.9	-8.0	20.0	26.1	26.1	43.3	-8.5	-2.4	3.7
M05-2X	7.7	-0.3	27.3	35.1	34.4	63.8	12.0	7.0	7.0
M06	13.7	0.0	25.1	28.3	31.9	58.5	9.1	5.3	5.4
M06-2X	7.8	-2.1	22.9	31.3	32.7	59.6	7.8	4.4	4.4
B2PLYP	-2.5	-9.1	14.0	27.8	27.7	52.9	-7.6	-2.5	2.9
ROB2PLYP	0.0	-8.2	16.0	28.9	28.9	53.3	-5.1	-1.2	1.7
MPW2PLYP	-1.0	-7.5	16.0	29.1	28.8	54.9	-6.1	-0.9	2.1
ROMPW2PLYP	1.0	-7.0	17.3	29.9	29.7	54.7	-4.1	0.0	1.9
ROMP2	16.6	7.9	30.5	46.8	46.4	57.5	18.1	13.3	13.3
SCS-ROMP2	-1.5	-8.5	13.3	28.5	27.6	46.3	-6.6	-3.3	3.3
SOS-ROMP2	-10.0	-15.9	5.4	19.8	18.6	42.4	-15.1	-10.9	10.9
CBS-QB3	53.1	1.2	24.9	37.3	37.8	62.0	48.0	15.1	15.1
G3(MP2)-RAD[31]	**5.1**	**-5.3**	**16.0**	**28.7**	**29.5**	**51.8**			

perform less in reproducing D($^\bullet$P-X). The benchmark values of the first group can be accurately reproduced using various low-cost procedures, whereas in case of the D($^\bullet$P-X) values large deviations (up to an average overestimation of 15.4 kJ/mol for the CN substituent) are obtained.

The differences between restricted and unrestricted results are for all investigated functionals rather small, amounting to 0-5 kJ/mol. This is in accordance with a recent detailed analysis by Menon and Radom investigating the effect of increasing HF exchange and corresponding spin contamination on bond dissociation energies.[66] Considering all substituents, the restricted version is in general preferred, however in the case of D($^\bullet$P-X) there is no clear preference between U and RO. The largest improvement using the restricted version is observed for the MPWB1K and B2PLYP functionals.

Table 3: Bond Dissociation Energies D($^{\bullet}$P-X), in kJ/mol. LD, MD and MAD, in kJ/mol, refer to the largest, mean and mean absolute deviation from the G3(MP2)-RAD values.

method X	C_6H_5	CN	OH	OCH_3	SCH_3	LD	MD	MAD
B3P86	35.7	154.0	117.9	42.2	-42.2	23.6	2.1	13.4
B3LYP	17.3	138.3	99.5	25.5	-62.2	-35.3	-15.7	18.9
ROB3LYP	17.1	139.5	101.4	27.5	-62.2	-35.5	-14.7	18.4
BMK	29.6	154.7	103.4	34.1	-53.0	24.3	-5.7	15.6
ROBMK	29.1	155.9	104.2	35.3	-54.4	25.5	-5.4	16.1
MPW1K	29.1	154.5	95.8	27.4	-52.4	24.1	-8.5	18.2
MPWB1K	35.2	153.4	104.2	34.9	-48.1	23.0	-3.5	13.2
ROMPWB1K	34.3	155.0	105.3	36.7	-49.5	24.6	-3.0	13.9
M05	19.5	125.3	108.2	35.8	-46.6	-33.1	-11.0	13.1
M05-2X	45.3	158.6	114.0	53.7	-42.3	28.2	6.5	10.3
M06	33.6	133.7	114.6	49.5	-36.8	-19.0	-0.5	7.8
M06-2X	37.5	145.1	110.5	51.8	-43.9	-15.1	0.8	8.4
B2PLYP	36.9	140.5	106.2	41.7	-52.1	-15.7	-4.8	10.2
ROB2PLYP	36.1	138.5	108.3	44.3	-51.4	-16.5	-4.2	9.7
MPW2PLYP	38.9	144.8	106.4	42.9	-51.5	14.4	-3.1	10.3
ROMPW2PLYP	37.8	143.1	108.4	45.4	-51.1	-14.8	-2.7	10.0
ROMP2	76.4	158.8	131.2	82.9	-28.4	31.7	24.8	24.8
SCS-ROMP2	53.7	145.7	110.3	62.0	-49.7	15.3	5.0	8.9
SOS-ROMP2	44.0	140.1	98.9	50.4	-60.0	-20.0	-4.7	8.6
CBS-QB3	64.7	135.8	114.2	58.9	-34.0	12.1	8.5	8.5
G3(MP2)-RAD[31]	**52.6**	**130.4**	**102.8**	**51.2**	**-40.0**			

Focussing on the D($^{\bullet}$P-C) values (Table 2), it is seen that ROB2PLYP performs the best, with an MAD of 1.7 kJ/mol. ROMPW2PLYP performs in a very similar way, with an MAD of 1.9 and MD of 0.0 kJ/mol. The unrestricted variants of these double-hybrid functionals also are in close agreement with the G3(MP2)-RAD method (MAD(B2PLYP) = 2.9 kJ/mol and MAD(MPW2PLYP) = 2.1 kJ/mol). The double-hybrids clearly outperform the B3LYP, B3P86 and MPWB1K functionals, although the ROMPWB1K gives good results with an MAD of 5.1 kJ/mol. The BMK and MPW1K also show very good agreements with the benchmark values. The more recent methods M05, M05-2X, M06 and M06-2X perform slightly less well, providing an LD value of 12.0 kJ/mol for M05-2X. Surprisingly, the M05 (parameterized including both transition metals and nonmetals) outperforms M05-2X (parameterized only for nonmetals). The more recent variants however show the expected trend as a slight decrease of the MAD is observed for M06 versus M06-2X (5.4 to 4.4 kJ/mol). ROMP2 shows the poorest agreement with G3(MP2)-RAD (MD = 13.3 kJ/mol). Whereas the ROMP2 method largely overestimates the benchmark values, the modified methods systematically show an underestimation. The modified methods demonstrate a substantial improvement, in particular the SCS-ROMP2 method leads to an MD of -3.3 kJ/mol and an acceptable LD of -6.6 kJ/mol for the phenyl substituent.

The analysis of the computed D($^{\bullet}$P-X) (Table 3) immediately shows that the benchmark values can only be marginally reproduced using the examined low-cost methods. None of the methods succeeds in reproducing the G3(MP2)-RAD values within an accuracy of 10 kJ/mol for all five substituents X. The benchmark level of theory was previously shown to provide accurate results for the calculation of radical heats of formation of small open-shell molecules. Henry et al. investigated 24 doublet radicals and 5 triplet biradicals for which reliable experimental data are available, resulting in an G3(MP2)-RAD MAD and MD of 4.0 and -2.0 kJ/mol, respectively.[67] For the present study, the BMK method was taken as a test example and radical heats of formation for the small open-shell systems under interest here were calculated (Table 4). The G3(MP2)-RAD method does succeed in reproducing the heats of formation in an accurate way for all molecules, whereas the low-cost BMK method fails for the substituents OCH_3, SCH_3 and CN. Due to cancelation of errors, calculated BDEs can often be better reproduced. However, the deviations obtained in this work (Table 3) are similar to those reported in a previous study of De Vleeschouwer and coworkers, studying the B3LYP, BMK and B3P86 levels of theory for a set of 89 radical combinations.[68] They observed reasonable performance for the BMK and B3P86 functionals, with an MAD value of 10.5 and 11.5 kJ/mol, respectively. Both functionals outperform the B3LYP functional (MAD of 24.1 kJ/mol).

Table 3 indicates that M06 and M06-2X perform overall the best, although large LD values are obtained in case of the phenyl substituent. The SOS- and SCS-ROMP2 methods turn out to be a good choice, with an MAD of 8.6 and 8.9 and MD of -4.6 and 5.0 kJ/mol, respectively. The

Table 4: Radical heats of formation at 0 K ($\Delta_f H_0^0$) for the open-shell radicals (substituents X), in kJ/mol.

method	Ph	CH_3	CN	OH	OCH_3	SCH_3
G3(MP2)-RAD[67]	343.0	147.1	434.4	34.3	27.8	126.8
UBMK	348.4	154.0	454.3	36.8	11.0	121.1
exp.	341.4[62]	150.0[69]	438.5[70]	36.9[62]	28.5[71]	131.4[62]

performance of the M05-2X method is also acceptable, even with an LD of 28.2 kJ/mol for the CN substituent whereas the results are much better for the other substituents. Considering the results for the phenyl substituent, it is seen that all DFT methods, incorporating the double-hybrids, largely underestimate the G3(MP2)-RAD value. The modified ROMP2 variants lead to substantially improved results, the SCS-ROMP2 method shows the best agreement (deviation of only 1.1 kJ/mol). For the OCH_3 and SCH_3 substituents, it is seen that the majority of the hybrid DFT functionals largely underestimate the benchmark values, however a good agreement is obtained for the M05-2X, M06 and M06-2X functionals. The double-hybrids also perform reasonably well. The computed CN substituent results on the other hand, are much higher than the G3(MP2)-RAD counterpart. For the hydroxyl substituent, all methods (with exception of B3P86 and ROMP2) perform well.

Our results demonstrate that the B3LYP method is outperformed by all of the contemporary methods, including the SCS-ROMP2 method. Albeit the double hybrid functionals perform somewhat better, the performance of the theoretical methods for the difficult class of phosphorus-containing molecules depends to a large extent on the involved substituent. The results illustrate that more phosphorus-containing species should be included in modern datasets used for benchmarking purposes. In order to achieve this goal accurate experimental data are needed. At present, 9 phosphorus-containing compounds, i.e., PH_2, PH_3, P_2, PF_3, PF_5, P_4, $POCl_3$, PCl_5, PCl_3, are included in the G3/99 test set.[72,73]

For the study of coke inhibiting additives, only the substituents CH_3, C_6H_5 and OCH_3 are of relevance. Based on it's good performance for radical reactions, we will systematically use the BMK functional (MAD = 10.2 kJ/mol) for further computations. This functional has the additional advantage of being well-suited for the computation of kinetic data as we demonstrated in particular for abstraction reactions,[74] which is also of high importance in the search for effective coke additives. Resulting from previous analysis, we also opt for the M05-2X, and SCS-ROMP2 methods as their MADs are found to be the smallest for the relevant substituents, corresponding to 4.4 and 4.7 kJ/mol, respectively.

Organophosphorus compounds

The reaction between phosphorus-containing additives and the coke surface is based on the decomposition products of the added phosphorus compounds. A set of 10 phosphorus-containing species is investigated, the structures are depicted in Figure 3. We consider 2 categories depending on the oxidation state of the phosphorus atom, i.e., phosphorus(III) (**1** to **7**) versus phosphorus(V) compounds (**8** to **10**). Molecules **2** (TPPn), **7** (TPP) and **10** (TPPO) represent industrially important additives (see Figure 1). Dissociation of the P-C, P-O or O-C bonds is considered leading to 13 different decomposition radicals (Figure 5). It is noted that in some cases a particular radical can be formed following different dissociations, i.e. the $^\bullet P(CH_3)_2$ compound (**11**) originates from the P-C dissociation of molecule **1** as well as from P-O dissociation of molecule **3**.

Geometries and atomic charges

The phosphorus(III) and phosphorus(V) compounds have a trigonal pyramidal and tetrahedral structure, respectively. Salient bond lengths and angles are taken up in the Supporting Information. It is found that the P-C, P-O and O-C bond lengths amount on average to 1.8, 1.6 and 1.4 Å, respectively. Detailed comparison between **1** and **8**, **5** and **9** as well as between **2** and **10** shows that the P-C and P-O bonds decrease slightly with changing oxidation state of the phosphorus atom. The effect of the phenyl versus the methyl substituent results in an increase in the P-O bond with 0.07 Å and a corresponding decrease in the O-C bond (comparison between **5** and **7**), whereas the

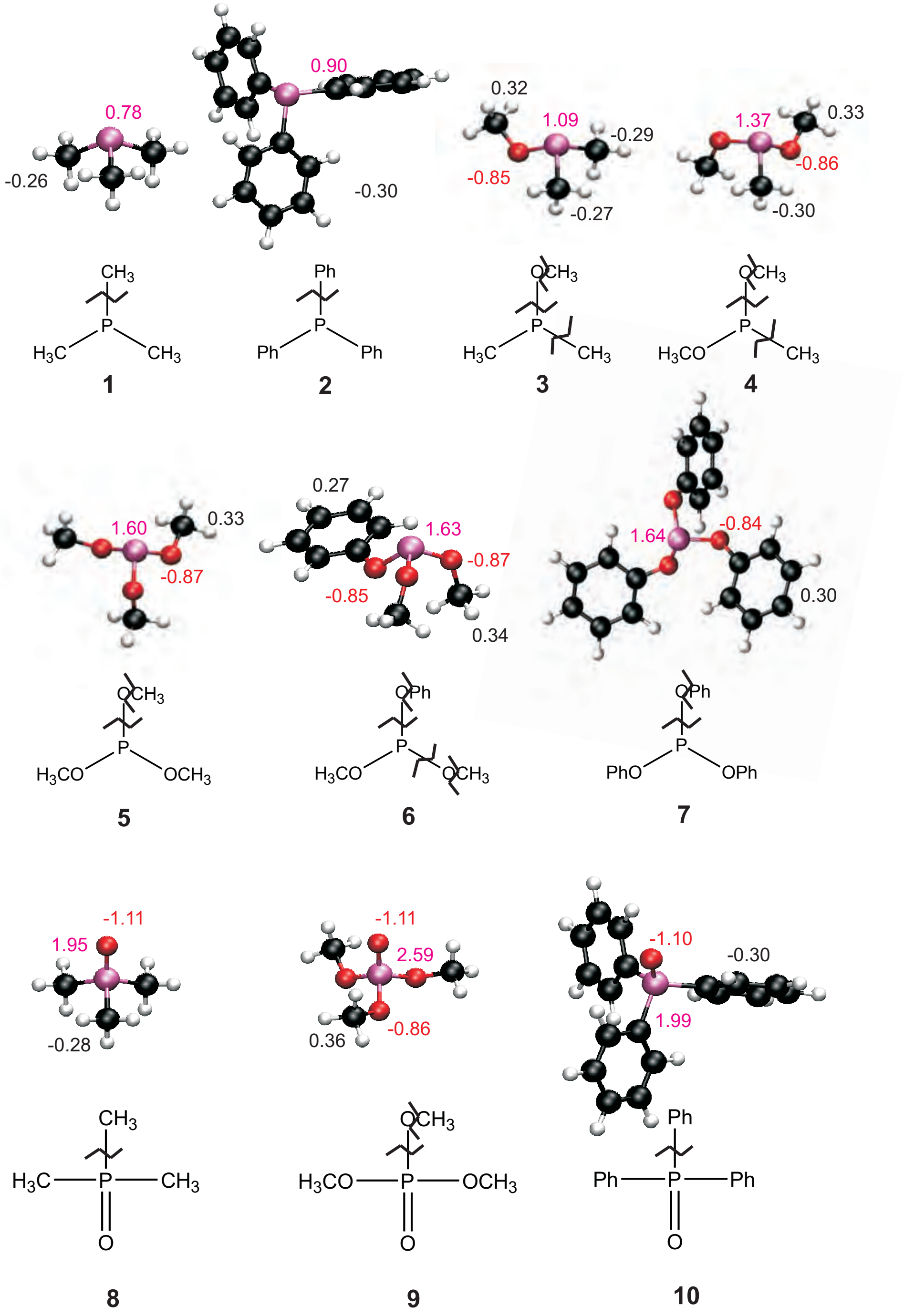


Figure 3: Set of 7 P(III)- and 3 P(V)-compounds. NPA charges, calculated at the BMK/6-311+G(3df,2p)//B3LYP/6-31+G(d,p) level of theory, are given.

P-C bond remains practically unaltered (**1** versus **2**, **5** versus **7**, and **8** versus **10**). The molecules under study exhibit various geometrical conformations due to internal rotations. The rotation of a methyl or phenyl group can be modeled as a free rotor, whereas rotation of a methoxy or phenoxy group can lead to rotational barriers of approximately 20 kJ/mol. A conformational study was performed on all molecules under investigation, treating all consecutive rotations one-dimensionally and uncoupled using the B3LYP/6-31G(d) level of theory. The rotational potentials are displayed in the Supporting Information.

Using the minimum energy configurations, atomic charges were computed using the natural population analysis (NPA) procedure,[75] the results are given in Figure 3. It is seen that the three bond types under study are all strongly polar in nature. It is furthermore clear that comparison between the corresponding phosphorus(III) and phosphorus(V) species shows that the charge separation in case of the P-C and P-O bond is more significant, suggesting an increase in BDEs for these dissociations. The O-C bond is unaffected. There is no significant effect of phenyl versus methyl substituent. Charge values are known to depend crucially on the population analysis used and therefore a comparison between atomic charges calculated using various schemes, i.e., Mulliken,[76] NPA,[75] MK[77,78] and Hirshfeld-I,[79] is illustrated in Figure 4 for molecules **5** and **14** (analogous results were found for all other molecules). The NPA scheme leads to the largest values, whereas the MK and Mulliken charges tend to be smaller. The Hirshfeld-I atomic charges lie between them, and are overall in best agreement with the NPA values. The Hirshfeld-I charges are calculated using an iterative approach to identify atoms in molecules and are known to reproduce charges that generate the electrostatic energy surface the best.[79] Very recently, the Hirshfeld-I charges were observed to be more stable toward conformational changes.[80]

An iso-surface of the spin density of the product radicals as well as atomic spin charges for the phosphorus and oxygen atoms are plotted in Figure 5. The results show that the atomic spin charge on the phosphorus atom is 0.9 and 0.7 for the phosphorus(III) and (V) species, respectively. It is seen that delocalization of the unpaired electron results in phosphorus-centered radicals, even in case of dissociation of an O-C bond. The presence of phenyl (as compared to methyl) groups

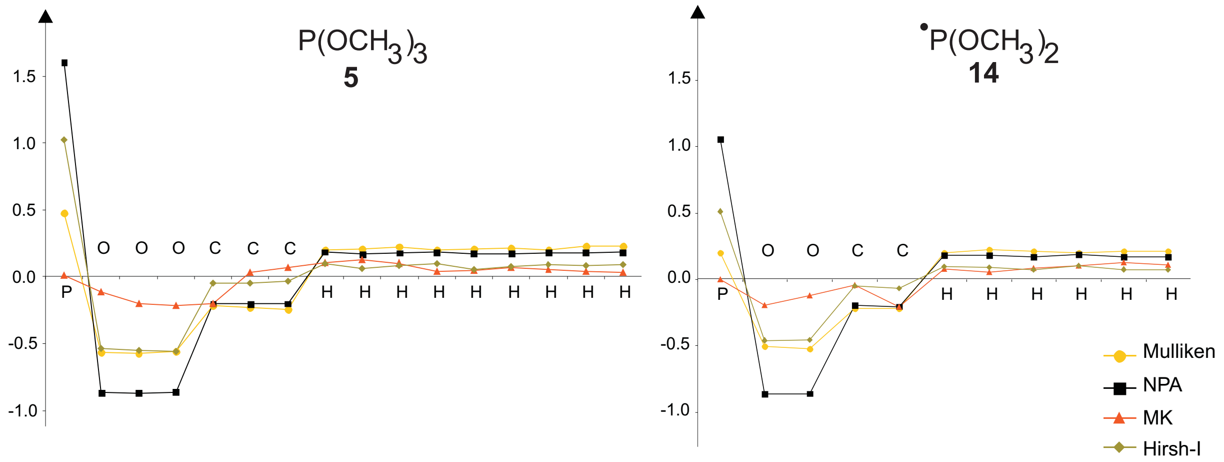


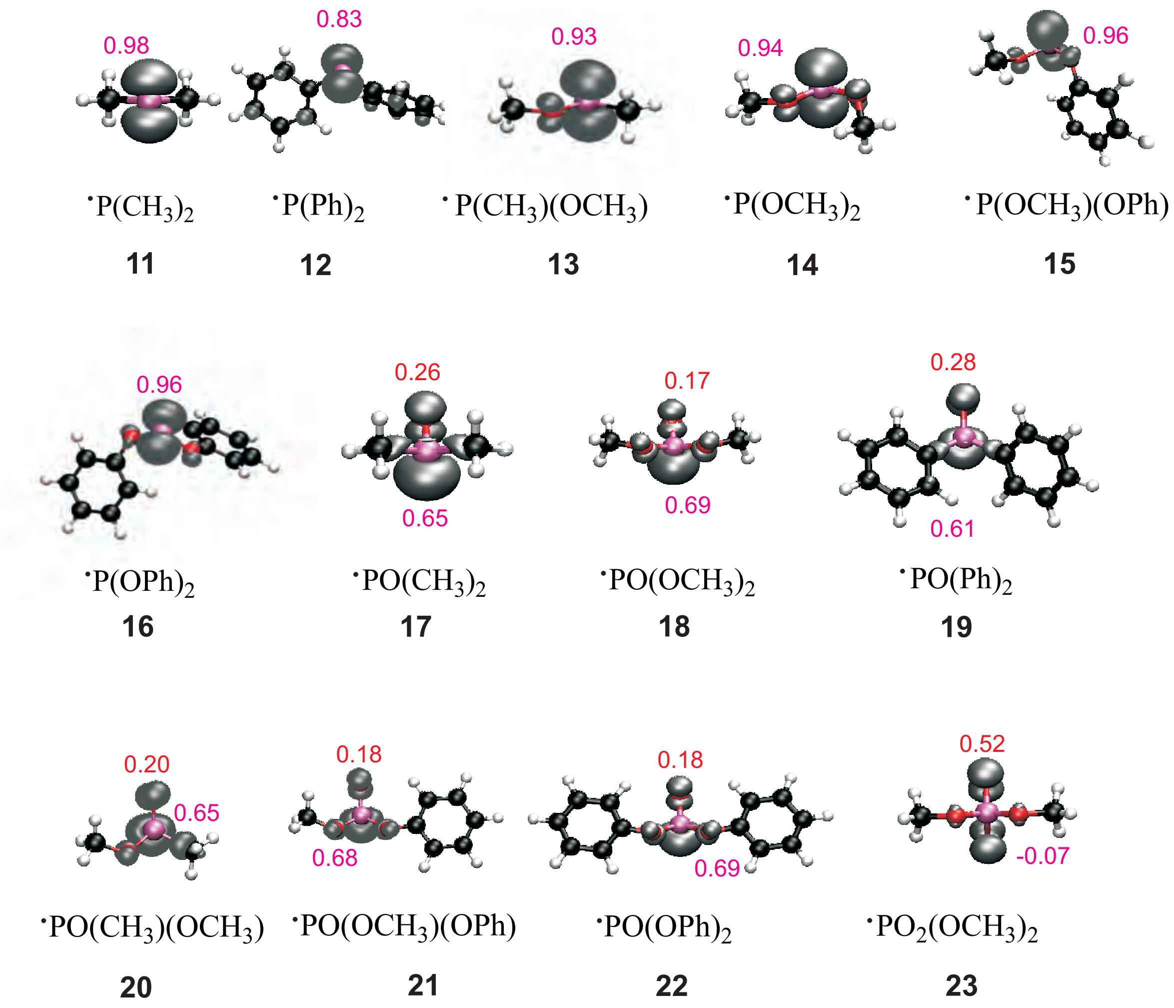
Figure 4: Comparison between Mulliken, NPA, MK and Hirshfeld-I atomic charges for the closed-shell molecule **5** and open-shell molecule **14**.

also results in a delocalization effect, as observed for compounds **12** and **19**. Radical **23** is the only one in which the unpaired electron is delocalized over the oxygen atoms only. The $< S^2 >$ values of the obtained radicals, calculated at the B3LYP/6-31+g(d,p), are given in Table 5. It is seen that there is no spin-contamination, as the deviations from the theoretical value of 0.75 are very modest.

Thermochemical properties

Standard enthalpies of formation, entropies and heat capacities of our set of 10 organophosphorus compounds and derived radicals (Figure 3 and Figure 5) are given in Table 5. All values are calculated using the harmonic-oscillator model using the optimized B3LYP/6-31+G(d,p) geometries. The performance of the BMK/6-311+G(3df,2p) level of theory is assessed by comparing our results with available experimental heats of formation. The calculated values are obtained using the atomization energy method, experimental enthalpies of formation of the gaseous atoms were taken from Curtiss et al.[81]

Comparison with the available experimental data indicates that the BMK/6-311+G(3df,2p)// B3LYP/6-31+G(d,p) level of theory is a suitable method for the computation of thermochemical data, as the deviations between experiment and theory amount to (in kJ/mol) -3.3 for **1**, 6.8 for **2**,



$^{\bullet}P(CH_3)_2$ **11**

$^{\bullet}P(Ph)_2$ **12**

$^{\bullet}P(CH_3)(OCH_3)$ **13**

$^{\bullet}P(OCH_3)_2$ **14**

$^{\bullet}P(OCH_3)(OPh)$ **15**

$^{\bullet}P(OPh)_2$ **16**

$^{\bullet}PO(CH_3)_2$ **17**

$^{\bullet}PO(OCH_3)_2$ **18**

$^{\bullet}PO(Ph)_2$ **19**

$^{\bullet}PO(CH_3)(OCH_3)$ **20**

$^{\bullet}PO(OCH_3)(OPh)$ **21**

$^{\bullet}PO(OPh)_2$ **22**

$^{\bullet}PO_2(OCH_3)_2$ **23**

Figure 5: Iso-surfaces (value 0.006 au) and Mulliken atomic values of spin densities of all phosphorus-containing radicals.

-6.6 for **5** and 15.1 for **8**. These values are moreover in very close agreement with the available G3X results reported by Dorofeeva and coworkers,[23,24] obtained at a higher computational cost. The results of Table 5 can serve as input in microkinetic models containing organophosphorus compounds, for benchmarking purposes of new functionals, etc.

Bond dissociation enthalpies

In this paragraph, bond dissociation enthalpies are reported and possible correlations with the bond lengths and charges are investigated.

Table 5: Enthalpies of formation, entropies and heat capacities, at 298 K (in kJ/mol), calculated at BMK/6-311+G(3df,2p)//B3LYP/6-31+G(d,p).

	ΔH_f^0	ΔH_{exp}^0	S^0	C_p^0		$<S^2>$	ΔH_f^0	S^0	C_p^0
1	-104.4	-101.1 ± 5.2[82]	316.5	105.9	**11**	0.7541	49.3	295.1	76.2
		-96.0 ± 4.0[83]			**12**	0.7634	316.3	445.6	184.6
2	332.8	326.0 ± 12.0[83]	551.4	270.6	**13**	0.7539	-144.0	334.1	88.8
		320.2 ± 4.7[82,84]			**14**	0.7540	-342.6	365.9	101.7
3	-287.1		363.0	119.8	**15**	0.7545	-228.6	437.8	158.3
4	-495.7		384.8	132.2	**16**	0.7548	-108.2	510.7	214.7
5	-712.2	-699.0 ± 8.0[83]	417.1	144.8	**17**	0.7542	-212.5	321.0	90.7
		-705.6 ± 6.2[82]			**18**	0.7534	-621.4	386.0	115.2
6	-592.6		492.4	201.5	**19**	0.7557	78.2	469.8	199.5
7	-353.5		646.5	314.3	**20**	0.7537	-423.6	352.0	103.0
8	-415.9	-434.4 ± 7.6[85]	337.3	120.4	**21**	0.7537	-499.6	455.0	171.6
		-431.0 ± 8.0[83]			**22**	0.7541	-371.9	529.6	28.3
9	-1067.6		433.2	155.6	**23**	0.7600	-846.2	399.4	130.4
10	38.8		571.0	284.1					

BDE values of structures **1** to **10** were computed at the BMK/6-311+G(3df,2p)) level of theory using B3LYP/6-31+G(d,p) geometries. These values are compared with M05-2X and SCS-ROMP2 results using the same basis set and optimized geometries. All results, including G3(MP2)-RAD results of some compounds, are presented in Figure 6 and can also be found in the Supporting Information. Experimental values for the dissociation of the P=O double bond of species **8** and **10** are known and can be compared with the theoretical predictions. The experimental values amount to 581.6 and 543.9 kJ/mol, respectively[86] and are fairly well reproduced by the BMK//B3LYP level of theory, yielding values of 560.6 and 543.1 kJ/mol. The SCS-ROMP2 BDE(P=O) value of compound **8** equals 577.3. These results again justify the use of the low-cost BMK//B3LYP method for the computation of BDE values of phosphorus-containing species. Comparison between the three methods shows that the qualitative trend in BDEs is unaltered. Substantial quantitative differences are however noticed, the overall ordering in BDEs is: BMK $<$ M05-2X $<$ SCS-ROMP2. The low-cost results are in good agreement with the computed G3(MP2)-RAD results. Overall it is found that the observed BDE trends do not correlate with geometrical parameters or atomic charges. Indeed, a clear correlation between bond lengths and BDE values is not obtained. This is in accordance with our previous results for a series of large aromatic species,[29] whereas a valid correlation was obtained by Zavitsas for a series of 41 typical carbon-carbon bonds (including single, double, triple, and highly strained bonds).[87]

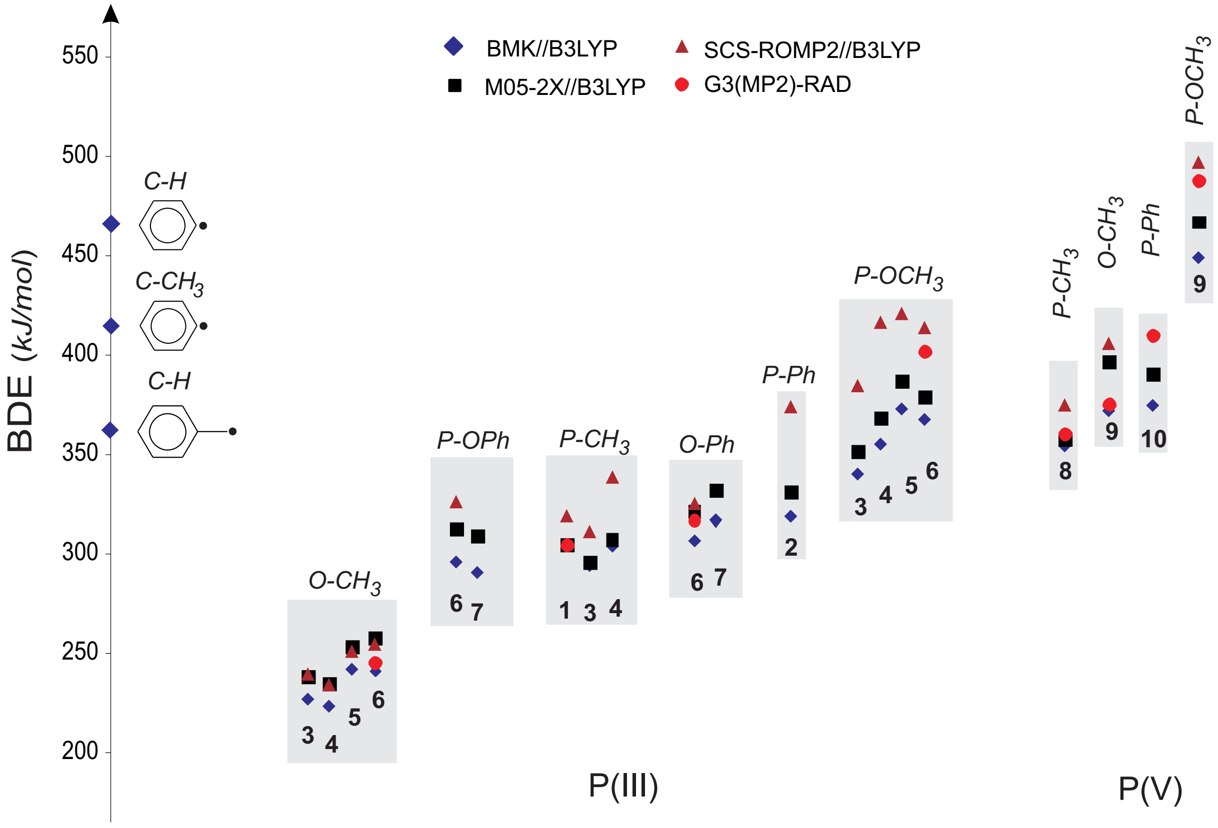


Figure 6: Bond dissociation enthalpies of the investigated organophosphorus compounds, using four levels of theory. C-H and C-C average values for benzyl and aryl radicals are also given.[29]

From Figure 6 it is observed that, as expected and in line with the charge distributions, the BDEs of the P(III)-molecules are lower than their corresponding P(V)-counterparts. Overall it is found that dissociation of a P-C bond requires more energy than dissociation of an O-C bond. The following order is obtained for the P(III)-species, being the largest subgroup of our test-set (Figure 6): BDE($O-CH_3$) $<$ BDE(P-OPh) $<$ BDE($P-CH_3$) $<$ BDE(O-Ph) $<$ BDE(P-Ph) $<$ BDE($P-OCH_3$). Compounds involving phenoxy-substituents will dissociate faster, as compared to methoxy-substituted species. Comparison between **1** and **2**, **5** and **7**, and **8** and **10** indicates that dissociation of the P-C and O-C bond is easier in case of a methyl substituent as compared to a phenyl substituent, whereas an opposite behavior is found for the dissociation of the P-O bond (the BDE(P-O) value is much lower in case of the larger phenyl groups). We note that the phosphorus atom has a crucial influence on the BDE trend, which can not be compared with the obtained radical stability trend in case of pure hydrocarbons. The present results are in line with the earlier observation that P-H and P-C BDEs are typically smaller than C-H and C-C BDEs due to a higher stability of the latter bonds.[31] Focussing on the subgroup of P-O and P-C dissociation, it is seen that the dissociation of a phenoxy group, corresponding with BDE(P-OPh, **7**) and BDE(P-OPh,**6**), requires the least amount of energy.

Our results indicate that although the BDE values provide valuable information regarding the thermodynamic behavior of the molecules under study, they can not be used as a primary indicator to assess the efficiency of phosphorus-containing additives. The industrially applied inhibitors **2**, **7** and **10** do not show peculiar dissociation properties when compared with the other molecules of our test set. Within this light, kinetic properties of reactions between the organophosphorus radicals and benzene are expected to be important and will therefore be investigated in a next study.

Conclusions

In the present study, thermodynamic properties of organophosphorus species have been investigated by means of theoretical computations.

First of all, we have investigated the performance of various contemporary DFT and modified ROMP2 methods to compute bond dissociation energies of phosphorus-containing species. It was shown that the composite G3(MP2)-RAD method generates heats of formation of small phosphorus-containing molecules which are in good agreement with experimental data. Phosphoranyl radicals with varying substituents X were taken as test set since benchmark G3(MP2)-RAD values were available. Both D($^\bullet$P-C) and D($^\bullet$P-X) values were computed. The benchmark values of the first group could accurately be reproduced using various low-cost DFT methods, whereas this was much more difficult for the second category. In case of D($^\bullet$P-C), the double-hybrid methods ROB2PLYP and ROMPW2PLYP perform the best, followed by the BMK and MPW1K. The D($^\bullet$P-X) values on the other hand, were overall best reproduced using the SOS- and SCS-ROMP2 method. The present assessment however indicates that there is a large dependency on the substituent used and that chemical accuracy can not be achieved for the entire test set with the available low-cost density functionals. The correct reactivity trends are nevertheless produced by all investigated methods.

Standard enthalpies of formation, entropies and heat capacities of a set of 10 organophosphorus species, representing coke-inhibiting additives, were computed using the BMK/6-311+G(3df,2p)//B3LYP/6-31+G(d,p) level of theory and can be used as input in single-event kinetic models. Bond dissociation enthalpies were calculated using the BMK, M05-2X and SCS-ROMP2 level of theory. The three methods give the same stability trend. No correlations between BDEs on one hand and geometrical parameters or atomic (spin) charges were obtained. The BDEs of the phosphorus(III) molecules were found to be lower than their phosphorus(V) counterparts. Overall the following ordering is found: BDE(P-OPh) $<$ BDE(P-CH_3) $<$ BDE(P-Ph) $<$ BDE(P-OCH_3). This study suggests, in accordance with experimental observations, that observed trends in the additive effectiveness towards coke inhibition are not dominated by differences in bond strengths.

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Supporting Information Available Tables S1 and S2 contain the xyz coordinates of the B3LYP/6-

31+G(d,p) optimized geometries of the organophosphorus molecules considered in this study. Geometrical parameters of molecules **1** to **10** are given in Figure S1. Figures S2 to S11 gives the rotational barriers for the methoxy- and/or phenoxy-substituents, calculated at the B3LYP/6-31G(d) level of theory. Table S3 contains the calculated BDEs using B3LYP/6-31+G(d,p) optimized geometries and BMK, M05-2X and SCS-ROMP2 energies in combination with the 6-311+G(3df,2p) basis set.

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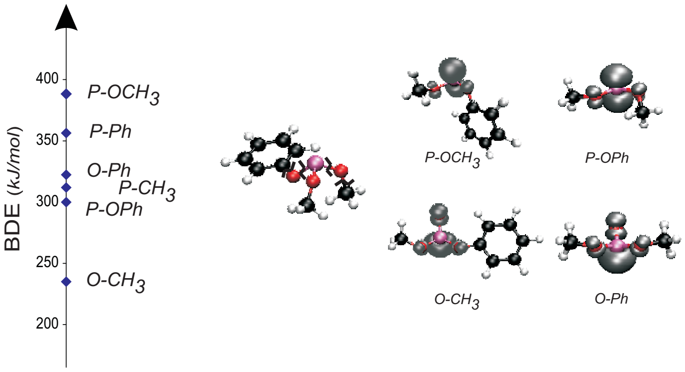

Figure 7: TOC figure.