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DENSITY FUNCTIONAL STUDY OF BOND DISSOCIATION ENERGIES IN HIGHLY BROMINATED DIPHENYL ETHERS

DAN MAFTEI[a], MIHAI DUMITRAȘ[a], DRAGOȘ-LUCIAN ISAC[a,b], ALIN-CONSTANTIN DÎRȚU[a,*]

ABSTRACT. Bond dissociation enthalpies (DEs) relevant to thermal dissociation of brominated diphenyl ethers were investigated in a computational approach at the density functional theory (DFT) level. In a preliminary assessment of eight of the most popular exchange-correlation functionals (including B3P86, PBE1PBE, mPW1PW91, wB97xD and two of each of the M05 and M06 families) the M06 meta-hybrid is shown to perform the best in reproducing two experimental C-O and C-Br BDEs, with errors bellow 1 kcal/mol and less dependent on basis set. The M06/cc-pVDZ is chosen as a good compromise between cost and accuracy for computing DEs of seven brominated diphenyl ethers. In the case of decabromodiphenyl ether we report a DE of 68.7 kcal/mol for the homolysis of the ether group and 74 to 77 kcal/mol for bromine cleavage. Compared to the corresponding values of the fully brominated compound, in lower brominated congeners we predict a substantial increase of both DEs with the decrease of bromine content.

Keywords: *brominated flame retardants, decabromodiphenyl ether, density functional theory, bond dissociation energies*

INTRODUCTION

Flame retardants (FRs) are materials that inhibit or resist the spread of fire that are added to polymers which are used in consumer goods [1,2]. There is limited knowledge about the mechanisms via which these chemicals migrate into and behave in the indoor environment and finally influence the human exposure to such compounds [3]. The estimation of human exposure to brominated FRs is based on reported levels for such compounds in several

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[a] *Department of Chemistry, "Alexandru Ioan Cuza" University of Iasi, Department of Chemistry, Carol I Blvd. No 11, 700506 Iasi, Romania*

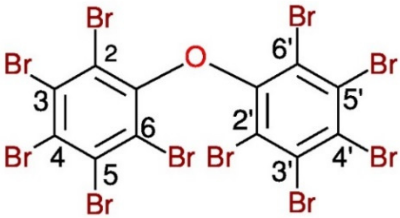
[b] *"Petru Poni" Institute of Macromolecular Chemistry Iasi, Grigore Ghica Voda Al. No. 41A, 700487 Iasi, Romania*

* *Corresponding author: alin.dirtu@chem.uaic.ro*

matrices like food or indoor dust [4]. Since higher elution temperatures are needed when applying conventional chromatographic techniques for their determination, FRs might undergo thermal degradation and therefore errors occur in their analysis [5] especially when targeting the highly brominated FRs such as polybrominated diphenyl ethers (PBDEs) and decabromodiphenyl ether (BDE 209) in particular. By the use of theoretical computations, it is possible to evaluate the most probable degradation products as well as the degradation mechanisms of selected brominated FRs.

In spite of their great importance, to the best of our knowledge there are only few experimental studies concerning the degradation of PBDEs, generally focused on photodegradation or reductive debromination mechanisms [6–8]. In contrast to the scarcity of experimental thermochemical data, PBDEs have inspired a large amount of computational work, the molecular structure of several species [9] as well as their dehalogenation (either photochemical [10] or reductive) leading to lower brominated congeners being the subject of several studies performed at levels ranging from semiempirical [11] to *ab initio* and Density Functional Theory (DFT) [12,13]. In effect, a consistent dataset of thermochemical parameters computed for PBDEs can be compiled from the literature of the last decade [14]. However, the lack of accurate experimental or even theoretical references regarding the thermochemistry of PBDEs, assumptions on their relative stability or reactivity, based on results of either semiempirical or DFT calculations, strongly reflect the particular parametrization (i.e. AM1, PM3, etc.) or the composition of the exchange-correlation functional, respectively. Although compound theoretical methods exist, including all-electron multi-reference computations and perturbational corrections to provide accurate thermochemical quantities regardless the nature of the compound of interest, most of them can hardly be applied to PBDEs in general and to highly brominated congeners in particular. Therefore, if one relays on DFT as a scalable alternative, the chosen density functional should account for the effects of electron correlation in an implicit manner.

In line with the above considerations, our study focused on the use of the DFT to model the bond dissociation energies (DEs) relevant to thermal decomposition of PBDEs including the fully brominated decabromodiphenyl ether (BDE 209, structure given in Scheme 1) and eight of the most abundant lower brominated congeners reported by previous literature for indoor dust samples [3,4].



Scheme 1. Structure of decabromodiphenyl ether (BDE 209)

Unlike previous DFT works on PBDEs, we have selected the exchange-correlation density functional from six of the most popular for computational thermochemistry [15–17] including B3P86, wB97xD, PBE0 [18], mPW1PW91 [19] as well as M05 [20] and M06 [21] as well as their double exchange M05-2X [22] and M06-2X variants, based on the accuracy in reproducing two experimental C–O and C–Br bond DEs.

RESULTS AND DISCUSSION

DEs for relevant bonds in bromobenzene (C_6H_5–Br) and diphenyl ether (C_6H_5O–C_6H_5), computed with each of the considered functionals in conjunction with eight basis sets are collected in Tables 1 and 2, respectively. First, it could be noticed the strong variation of the computed values with the exchange-correlation functional, with up to 8-12 kcal/mol (10-15%) discrepancy between M05 values, the lowest overall, and the double exchange M05-2X counterparts. In addition, values computed with the same two functionals are in qualitative disagreement, the later (M05-2X) foreseeing a DE for the C_6H_5O–C_6H_5 bond at 3 kcal/mol below the corresponding value for the C_6H_5–Br, whereas the M05 functional reproduces the same quantities in the reverse order.

Table 1. C_6H_5–Br bond dissociation enthalpies (in kcal/mol, at 298.15K) computed at different DFT levels

	Exchange-correlation functional							
Basis set	**M05**	**M05-2X**	**M06**	**M06-2X**	**B3P86**	**PBE0**	**mPW1PW91**	**wB97xD**
6-311G(d)	74.1	85.6	79.6	86.1	79.0	78.9	77.0	81.6
6-311+G(d)	72.5	84.6	78.4	85.0	77.9	77.7	75.9	80.4
6-311+G(d,p)	72.7	84.7	78.6	85.0	78.1	77.9	76.0	80.5
6-311++G(d,p)	72.6	84.6	78.5	84.9	78.0	77.8	76.0	80.4
cc-pVDZ	75.6	86.7	80.6	87.7	80.2	80.0	78.1	82.7
cc-pVTZ	74.2	86.1	80.1	86.3	79.5	79.3	77.3	81.8
aug-cc-pVDZ	73.3	86.0	80.2	86.3	78.9	78.5	76.7	81.7
aug-cc-pVTZ	73.3	86.1	80.1	86.3	78.9	78.5	76.7	81.5

While the eight functionals considered generally disagree, even on the ordering of the two bond DEs, values computed with each of the functionals are almost independent on the basis set. In the case of the first four (Pople) basis sets, further addition of diffuse and/or polarization functions to the 6-311G(d)

Table 2. $C_6H_5O–C_6H_5$ bond dissociation enthalpies (in kcal/mol, at 298.15K) computed at different DFT levels

	Exchange-correlation functional							
Basis set	**M05**	**M05-2X**	**M06**	**M06-2X**	**B3P86**	**PBE0**	**mPW1PW91**	**wB97xD**
6-311G(d)	73.8	81.3	77.1	78.4	80.5	79.8	78.3	79.4
6-311+G(d)	73.6	81.2	76.9	78.2	80.4	79.7	78.2	79.3
6-311+G(d,p)	73.6	81.2	76.9	78.2	80.4	79.7	78.2	79.3
6-311++G(d,p)	73.6	81.2	76.9	78.2	80.4	79.7	78.2	79.3
cc-pVDZ	74.9	82.2	77.8	79.8	81.0	80.3	78.8	80.1
cc-pVTZ	75.1	82.6	77.9	79.1	81.3	80.6	79.0	80.2
aug-cc-pVDZ	74.9	82.6	78.0	80.1	81.2	80.5	79.0	80.3
aug-cc-pVTZ	74.9	82.7	77.8	79.1	81.3	80.5	79.0	80.2

yields C–Br DEs up to 1 kcal/mol lower and has essential no effect (-0.2 kcal/mol) on C–O DEs. Using correlation-consistent (cc, Dunning) basis sets result in even lower differences, DEs computed at DFT/aug-cc-pVTZ being less than 0.5 kcal/mol apart from the corresponding values computed using the cc-pVDZ basis set, the latter at a substantially reduced cost. Provided the methodology adopted in computing DEs (see Experimental Section, *Computational protocols*), prone to basis set incompleteness or superposition errors, ensuring that values computed are essentially converged values with respect to the basis set size is of particular importance. Therefore, from a methodological perspective, we emphasized that using either the cc-pVDZ or the aug-cc-pVDZ variant, the latter at a substantial cost when used on highly brominated systems, should provide converged DEs in conjunction with any of the above functionals.

Finally, to assess the accuracy of each density functional one needs to compare the computed DEs with the experimental values of either 80 kcal/mol [23] or 80.3 kcal/mol [24] reported for the corresponding C–Br bond and 77.8 kcal/mol [24] for C–O, respectively. Differences between computed and experimental DEs are graphically presented in Figure 1. For the C–Br bond we choose the recent value of 80.3 kcal/mol. One may note the sharp discrepancies of M05 and M05-2X values that underestimate and overestimate, respectively, the experimental quantities with up to 7-8 kcal/mol (10%). In addition, the M05, PBE0 and mPW1PW91 functionals reverse the order of the two bond DEs, B3P86 and M06-2X recover the two bond DEs values with different accuracy, whereas including dispersion corrections (as in wB97xD) improves marginally the computed DEs.

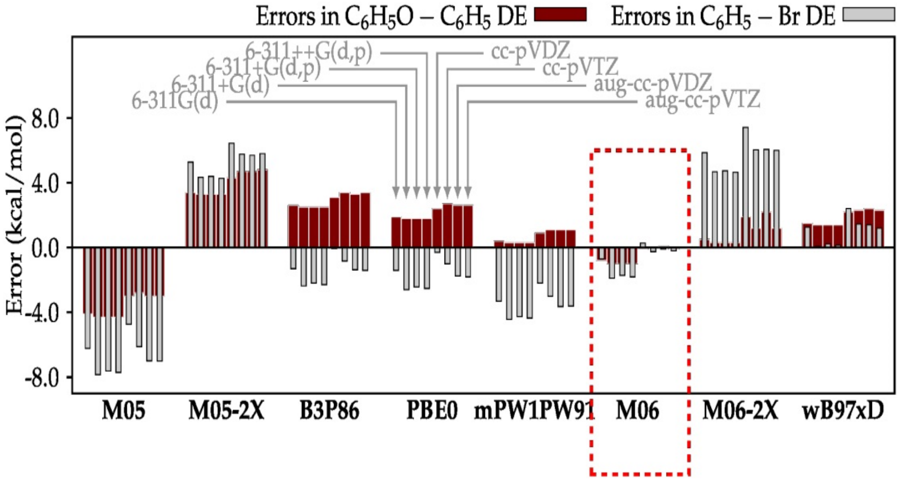


Figure 1. Differences (in kcal/mol) between computed C_6H_5–Br and C_6H_5O–C_6H_5 bond DEs and experimental counterparts

Among the selected functionals, the accuracy required in modeling the two bond DEs (2.5 kcal/mol apart) is achieved by M06 when used with any of the correlation-consistent cc-pV*n*Z basis sets. M06/cc-pVTZ values are within 0.1-0.2 kcal/mol of their experimental counterparts, but chemical accuracy (< 1 kcal/mol deviation) is achieved already at M06/cc-pVDZ, with a substantially reduced computational effort. Therefore we have further assumed comparable accuracy of the latter in modeling the C–O and C–Br bond energetics in PBDEs.

Table 3. Selected bond lengths (Å), valence and torsion angles (°) in BDE 209, computed at M06/cc-pVDZ level *vs.* experimental data

	Parameter	Computed	Experimental	
			Ref. [25]	Ref. [26]
Bond lengths	C_1-O	1.363	1.397	1.386
	C_2-Br	1.888	1.894	1.879
	C_3-Br	1.885	1.887	1.877
	C_4-Br	1.887	1.901	1.885
Valence angles	C_1-O-$C_{1'}$	125.0	120.9	120.7
	C_2-C_1-O	123.8	125.8	124.7
Torsion angle	C_2-C_1-O-$C_{1'}$	49.7	47.5	46.2

In Table 3 we compared a subset of internal coordinates from the geometry of BDE 209, optimized at M06/cc-pVDZ level in gas phase, with average experimental (XRD) values from selected references. Excepting the notable underestimation of the C–O bond (-0.2 to -0.3 Å), which may result in overestimated DE, and the 4° overestimation of the C–O–C angle, most of the remaining internal coordinates were reproduced within experimental uncertainties, in spite of the fact that M06 functional is not generally regarded as providing accurate geometries.

In a thermal decomposition scenario, degradation of highly brominated PBDEs may be initiated by either a debromination step, that explain the formation of nona-brominated congeners, the homolysis of C–O bond yielding brominated phenols or both. Energetics of the two pathways, as standard bond DEs computed at M06/cc-pVDZ level, is depicted in Figure 2. Compared to the DE computed for the corresponding bond in dyphenyl ether, our computations foresee a 9 kcal/mol weaker C–O bond in BDE 209. This may be rationalized on the basis of mutual repulsion between the bromine atoms in position adjacent to the ether group, but also considering the additional stabilization of the resulting brominated radicals compared to the unbrominated analogues [27]. In contrast, C–Br bonds are predicted at only 4-6 kcal/mol lower DEs in BDE 209 than in diphenylether. The computed 5-8 kcal/mol difference between the energetics of the C–Br and C–O bonds may be however underestimated, on the basis of an anticipated overestimation of the latter (see above). Hence, while most of the previous studies emphasize on debromination, photo-oxidation and subsequent intramolecular processes [27–29] in lower brominated PBDEs, results reported herein suggest that thermal decomposition toward polybrominated phenoxyl radicals and polybrominated phenyls is slightly favored in decabrominated diphenyl ether. However, the overall thermal decomposition mechanism may be influenced by several other factors, including radical stabilization or bimolecular steps not considered in our current approach.

Figure 3 depicts C–O and C–Br bonds DEs computed at the same M06/cc-pVDZ level of theory for six PBDE congeners: 2,2’,3,3’,4,4’,6,6’-octabromodiphenyl ether (BDE 197), 2,2’,3,4,4’,5’,6-heptabromodiphenyl ether (BDE 183), 2,2’,4,4’,5,5’-hexabromodiphenyl ether (BDE 153), 2,2’,4,4’,5,6’-hexabromodiphenyl ether (BDE 154), 2,2’,4,4’,5-pentabromodiphenyl ether (BDE 99), 2,2’,4,4’,6-pentabromo-diphenyl ether (BDE 100), 2,2’,4,4’-tetrabromodiphenyl ether (BDE 47) and 2,4,4’-tribromodiphenyl ether (BDE 28). The above mentioned PBDE congeners were selected based on previous literature on their levels reported for indoor dust samples, one of the most important matrices when addressing human exposure to such compounds, while together with BDE 209 they generally consist of more than 95% of the total PBDEs measured in such samples [3,4].

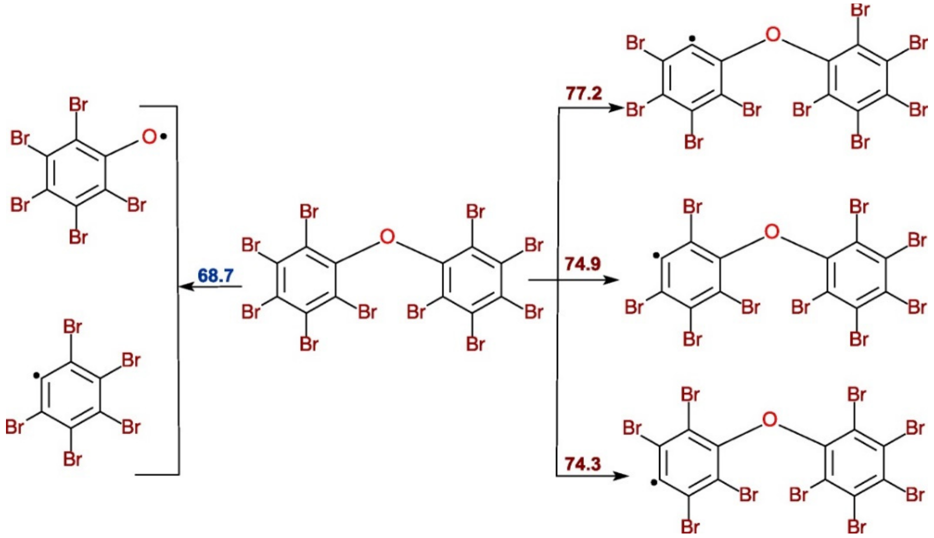


Figure 2. Differences (in kcal/mol) between computed C_6H_5–Br and C_6H_5O–C_6H_5 bond DEs and experimental counterparts

Values predicted for the C–O and C–Br bond DEs may be rationalized not only on the basis of bromine content, but also of the position of bromine atoms on the two rings. The overall trend shows that C–O bonds strengthens with the reduction of bromine content, from less than 70 kcal/mol in BDE 209 (see Figure 2) or about 70 kcal/mol in octa-brominated BDE 197 to more than 77 kcal/mol in the tri-brominated congener BDE 28. However, in asymmetric congeners the two C–O bonds do not follow the same trend. For instance, the homolytic cleavage of the C–O bond leading to 2,4,5-tribromo-phenyl radical is slightly favored to that leading to 2,4,5-tribromo-phenoxyl, the result being most likely related to a different stabilization energy of the two radicals. In the case of C–Br bonds, while the overall variation show a similar trend, the lower the number of bromine atoms, the higher the DE, mutual repulsion between bromine atoms in adjacent positions appears to weaken the corresponding C–Br bond with up to 6 kcal/mol when compared to the anticipated values. Given the smaller differences between C–Br and C–O bond DEs in congeners with lower bromine content it results in comparable strengths for the two bonds. However, regardless of the ordering of the two bond DEs, in deriving a kinetic model for the thermal decomposition of PBDEs one should account for the multiplicity of the C–Br bonds.

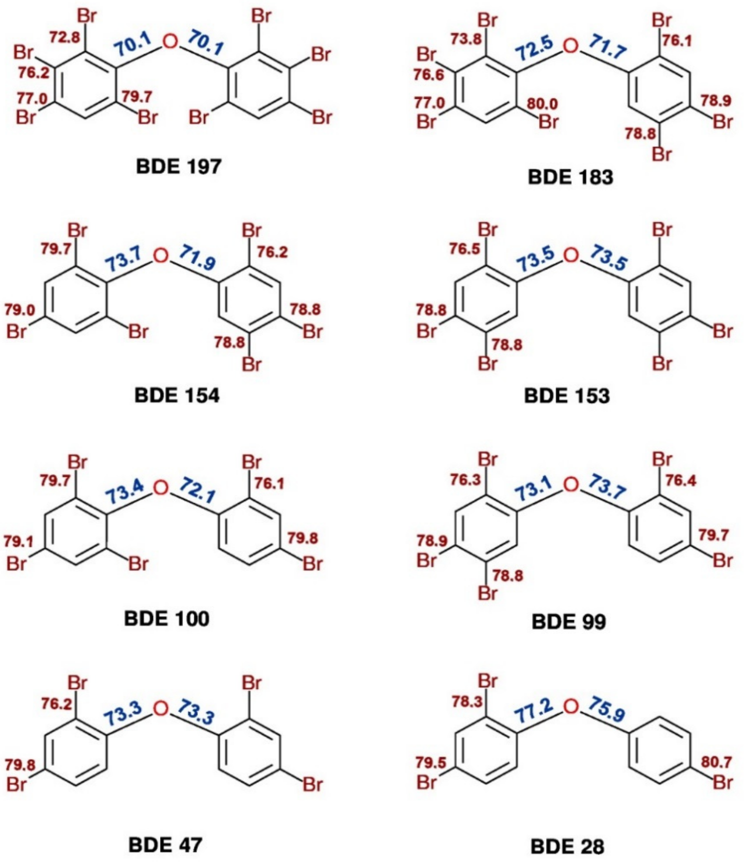


Figure 3. Bond DEs for C–O and C–Br (in kcal/mol) of selected PBDE congeners computed at M06/cc-PVDZ level in gas phase

CONCLUSIONS

Given the relatively low number of studies to report on the experimental thermochemical data concerning the PBDEs, we limit out conclusion to qualitative aspects derived from comparing the energetics of the two bond types, C–O and C–Br, of anticipated relevance for their thermal decomposition. We have shown that some of the most popular exchange-correlation density functionals, few of them used previously in computational works on PBDEs, show large deviations form experimental data on model compounds. Hence, some of the conclusions derived from absolute quantitative predictions at respective levels of theory, notoriously the M05 and M05-2X functionals, may need to be reevaluated. Bond dissociation energies computed at the M06/cc-pVDZ level, recommended by our work for computational thermochemistry of PBDEs, suggest that thermal decomposition of highly brominated congeners may result in polibrominated phenols and polibrominated benzene, whereas the debromination is prefered in the case of lower brominated congeners. These findings represent valuable information for the environmental studies focusing on the human exposure sources to PBDEs, but also to their corresponding degradation products, when screening methods might be systematically adjusted based on information provided by combined theoretical studies and thermal degradation experiments performed on selected target molecules.

EXPERIMENTAL SECTION

Computational protocols

All electronic structure calculations were performed using Gaussian 09 rev. C01 [30] running on a local cluster. Equilibrium geometries of all species, including radicals, were computed in the Unrestricted Kohn-Sham (UKS) formalism of the Density Functional Theory (DFT) in gas phase. Unconstrained geometry optimizations were performed using standard “tight” convergence criteria in both self-consistent field and geometry cycles and “ultrafine” integration grids. Harmonic vibrational frequencies computations were run subsequent to each optimization, in order to confirm, on one hand, the nature of the located stationary point and to perform further calculation of thermochemical parameters, on the other. Frequencies used in evaluation of zero-point vibrational energy were unscaled. Unless noted otherwise, standard bond dissociation enthalpies were calculated by subtracting the enthalpy of the molecule of interest from the sum of enthalpies of the two fragments, each at the corresponding equilibrium geometry of the lowest-energy electronic state.

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REFERENCES

[1]. World Health Organization / International Classification for Patient Safety (WHO / ICPS). *Environmental Health Criteria 162:* Brominated Diphenyl Ethers. Geneva: World Health Organization, **1994**.

[2]. World Health Organization / International Classification for Patient Safety (WHO / ICPS). Environmental Health Criteria 192: Flame Retardants-General Introduction. Geneva: World Health Organization; **1997**.

[3]. A. Covaci, S. Harrad, M.A.E. Abdallah, N. Ali, R.J. Law, D. Herzke, C.A. de Wit, *Environment International*, **2011**, *37*, 532.

[4]. A.C. Dirtu, N. Ali, N. Van den Eede, H. Neels, A. Covaci, *Environment International*, **2012**, *49*, 1.

[5]. A.C. Dirtu, M.A.E. Abdallah, A. Covaci, *Trends in Analytical Chemistry*, **2013**, *43*, 189.

[6]. Y. Shih, C.K. Wang, *Journal of Hazardous Materials*, **2009**, *165*, 34.

[7]. Y. Pan, D.C.W. Tsang, Y. Wang, Y. Li, X. Yang, *Chemical Engineering Journal*, **2016**, *297*, 74.

[8]. G. Rotko, P.P. Romańczyk, S.S. Kurek, *Electrochemistry Communications*, **2013**, *37*, 64.

[9]. J. Hu, L. Eriksson, Å. Bergman, E. Kolehmainen, J. Knuutinen, R. Suontamo, X. Wei, *Chemosphere*, **2005**, *59*, 1033.

[10]. L. Pan, W. Bian, *ChemPhysChem*, **2013**, *14*, 1264.

[11]. Y. -Y. Zhao, F. -M. Tao, E.Y. Zeng, *Chemosphere*, **2008**, *70*, 901.

[12]. M. Grabda, S. Oleszek-Kudlak, E. Shibata, T. Nakamura, *Journal of Molecular Structure: THEOCHEM*, **2007**, *822*, 38.

[13]. J. Zhou, J. Chen, C.H. Liang, Q. Xie, Y.N. Wang, S. Zhang, X. Qiao, X. Li, *Environmental Science and Technology*, **2011**, *45*, 4839.

[14]. J. Luo, J. Hu, X. Wei, L. Fu, L. Li, *Chemosphere*, **2015**, *131*, 17.

[15]. Y.G. Lazarou, A.V. Prosmitis, V.C. Papadimitriou, P. Papagiannakopoulos, *Journal of Physical Chemistry A*, **2001**, *105*, 6729.

[16]. X. Q. Yao, X.J. Hou, H. Jiao, H.W. Xiang, Y.W. Li, *Journal of Physical Chemistry A*, **2003**, *107*, 9991.

[17]. G.A. DiLabio, D.A. Pratt, *The Journal of Physical Chemistry A*, **2000**, *104*, 1938.

[18]. C. Adamo, V. Barone, *The Journal of Chemical Physics*, **1999**, *110*, 6158.

[19]. C. Adamo, V. Barone, *The Journal of Chemical Physics*, **1998**, *108*, 664.

[20]. Y. Zhao, N.E. Schultz, D.G. Truhlar, *The Journal of Chemical Physics*, **2005**, *123*, 161103.

[21]. Y. Zhao, D.G. Truhlar, *Theoretical Chemistry Accounts*, **2008**, *120*, 215.

[22]. Y. Zhao, N.E. Schultz, D.G. Truhlar, *Journal of Chemical Theory and Computation*, **2006**, *2*, 364.

[23]. D.F. McMillen, D.M. Golden, *Annual Review of Physical Chemistry*, **1982**, *33*, 493.

[24]. "CRC Handbook of Chemistry and Physics". CRC Press: Boca Raton, **2007**.

[25]. J. Eriksson, L. Eriksson, E. Jakobsson, *Acta Crystallographica Section C Crystal Structure Communications*, **1999**, *55*, 2169.

[26]. A.A. Mrse, S.F. Watkins, F.R. Fronczek, *Acta Crystallographica Section C Crystal Structure Communications*, **2000**, *56*, e576.

[27]. G. Rotko, P.P. Romańczyk, G. Andryianau, S.S. Kurek, *Electrochemistry Communications*, **2014**, *43*, 117.

[28]. M. Altarawneh, B.Z. Dlugogorski, *The Journal of Physical Chemistry A*, **2014**, *118*, 9338.

[29]. M. Altarawneh, B.Z. Dlugogorski, *Environmental Science and Technology*, **2013**, *47*, 5118.

[30]. M.J. Frisch, G.W. Trucks, H.B. Schlegel *et al.*, *"Gaussian 09 Revision C.01"*, Wallingford CT, **2009**.