DFT on Atmospheric Chemistry

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Overview

- Background
- Methods
- Applications

Some examples

- Flourine oxides (CPL,287,1998)
- CF_3OH (CPL,277,1997)
- Hydrofluorcarbons (CPL,403,2005)
- HSO radical(I.J.Q.C.,80,2000)
- POP (furans and their precursors)

Persistent Organic Pollutants

- **POP**s are organic compounds that are resistant to environmental degradation through **chemical, biological, and photolytic** processes.
- High Toxicity
- Bioaccumulation
- Diabetes
- Persistence on environment

POPs

- Some examples :

  Aldrin Dioxins Furans Chlordane

  PCB DDT Heptachlor

  Dieldrin Endrin Mirex HCB

- From :

- Pesticides
- Combustion (forestal, waste, hospital)

Experimental data

- Dangerous
- Problems with incomplete Cl combustion
- Sample impurity
- Lack of vibrational frequencies
- Variety of compounds
- Uncertainty in entalphy in phase transition

Density Functional Theory

- Hohenberg & Kohn ,Phys. Rev. 136 B 864 (1964)

  n(r) → V(r) → Electronic Properties

- Solve by Kohn & Sham ,Phys. Rev. 140 A 1133 (1965)

$$V_{\mathrm{eff}} = V_{\mathrm{H}} + V_{\mathrm{xc}} + V_{\mathrm{ext}}$$

Our work

- Six functionals
  - B3LYP, B3PW91, Mpw1pw91, B98
  - PBE, PBE0

- 2 basis sets
  - 6-311++G(3df,3pd)
  - 6-311++G(3d2f,3pd)

Isodemic Reactions

- An **isodesmic reaction** is a chemical reaction in which the number and type of chemical bonds and lone pairs are conserved in each side of the reaction.
- We obtain enthalpies theoretically, heat of reaction,so together with experimental heat of formation deduce interesed spieces.

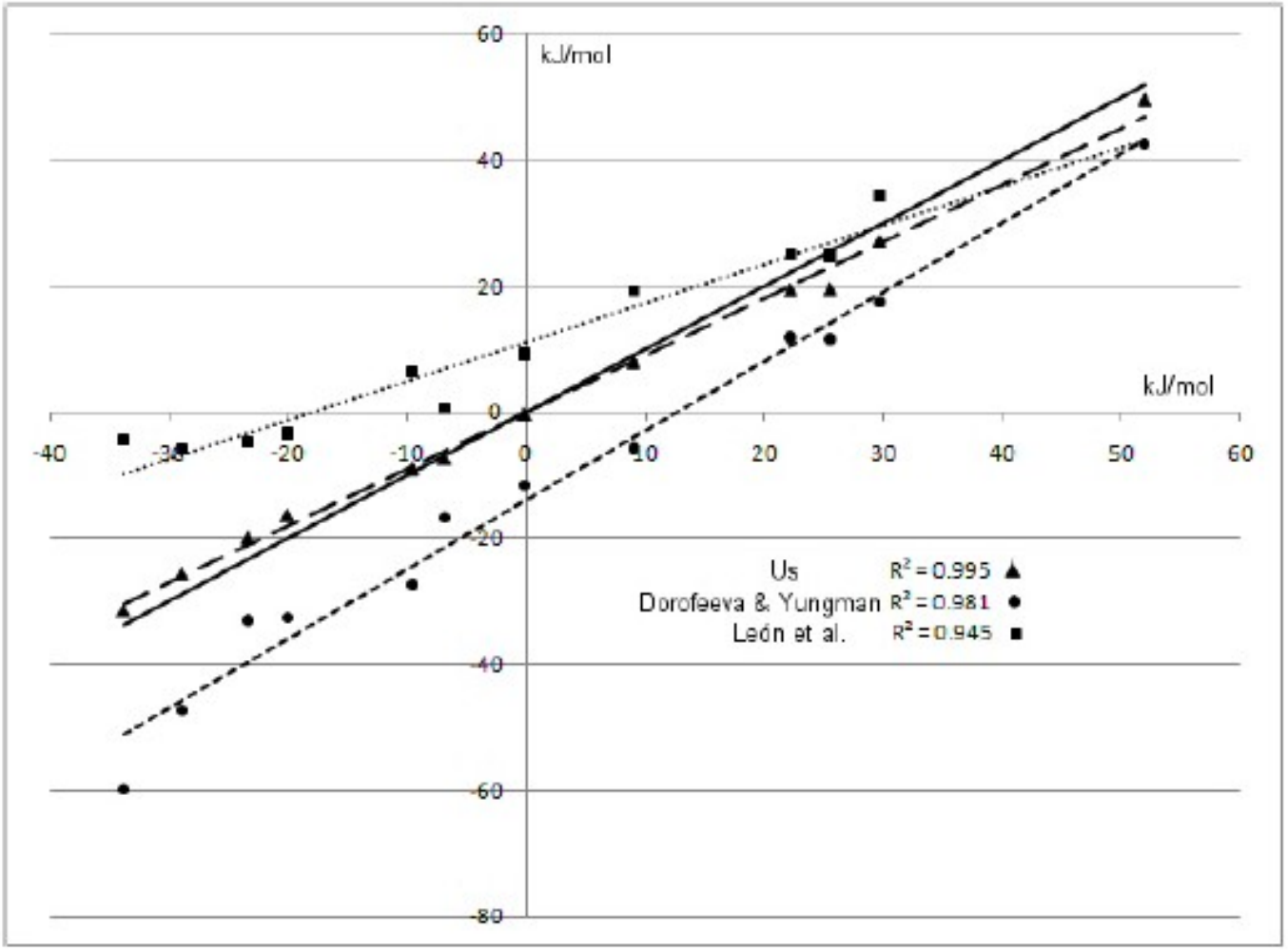
Chlorobenzenes

$$C_6H_6 + nCH_xCl_{4-x} \rightarrow C_6H_yCl_{6-y} + \text{C1 species}$$

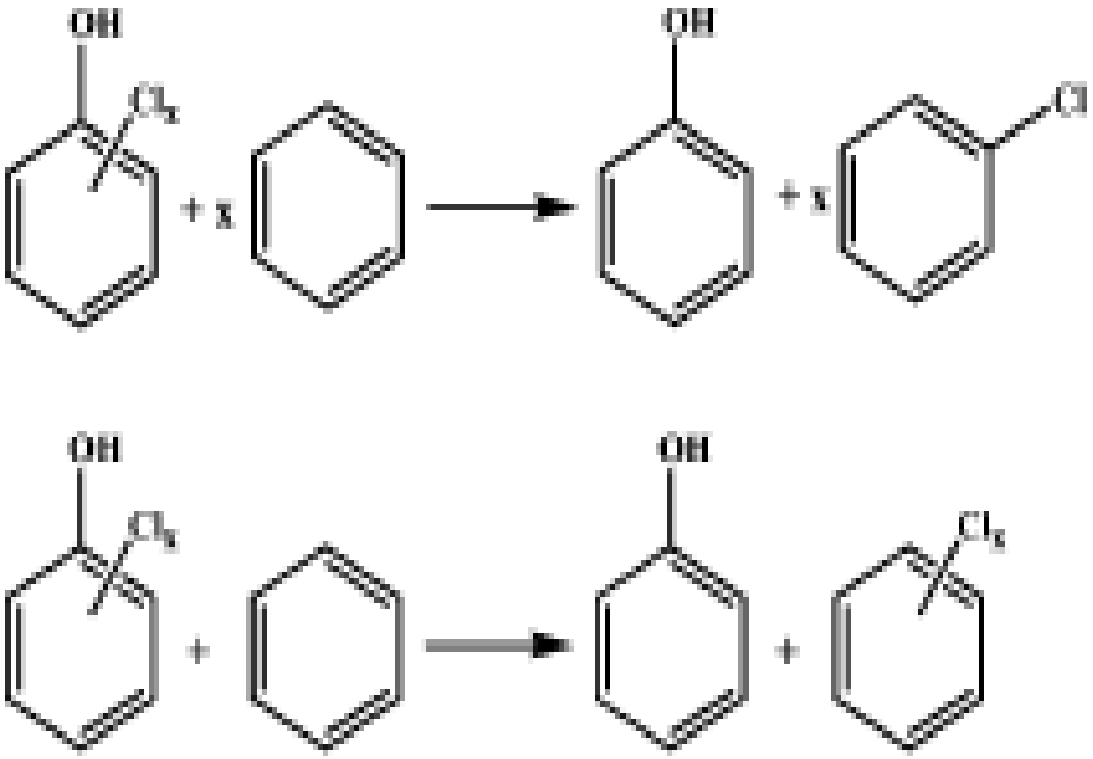
Species	NIST-TRC[a]	Pedley *et al*[b]	Cox & Pilchner[c]	Yan *et al*[d]	León *et al*[e]	Zhu & Bozzelli[f]	Dorofeeva & Yungman[g]	This work[h]
MCB		52.0±1.3					42.6	49.4±2.5
12DCB	29.7	30.2±2.1	29.7±1.6		34.0±2.0	34.1±3.9	17.4	26.9±2.5
13DCB	25.5	25.7±2.1	25.5±2.1		24.6±2.0	24.7±3.9	11.6	19.4±4.5
14DCB	22.2	22.5±1.5	22.2±1.3		24.8±2.0	24.7±3.9	11.9	19.3±4.5
123TrCB	9.0			8.2±1.8	19.2±2.5	19.5±6.4	-5.8	7.9±6.4
124TrCB	-0.2			4.9±1.6	9.1±2.5	9.4±6.4	-11.5	-0.3±6.4
135TrCB	-6.9			-2.6±1.4	0.6±2.5	0.6±6.4	-16.7	-7.3±6.4
1234TCB	-9.6				6.2±2.9	6.5±8.9	-27.3	-9.0±6.1
1235TCB	-20.1				-3.4±2.9	-3.1±8.9	-32.6	-16.3±6.1
1245TCB	-23.4				-4.8±2.9	-4.3±8.9	-33.0	-19.9±10.9
PCB	-29.0				-5.9±3.2	-4.1±11.4	-47.2	-25.6±5.1
HCB	-33.9	-35.5±9.4	-36.0±9.6		-4.5±3.5	-2.6±13.9	-59.8	-31.4±4.5
MAD[i]					12.6	12.0	13.8	2.5
Max. Error[i]					29.4	31.3	25.9	6.1

[a)]from ref.[294] [b)]from ref.[501] [c)]from ref.[502] [d)]from ref.[503] [e)]from ref.[474] [f)]from ref.[294] [g)]from ref.[479] [h)]PBE/6-311++G(3d2f,3pd) calculations, error bars are taken as two times the standard error of the averaging procedure. [i)]Mean absolute deviation with respect to the NIST-TRC values, except for MCB for which Pedley's value was used [j)]Maximum error with respect to the experimental values

Chlorobenzenes



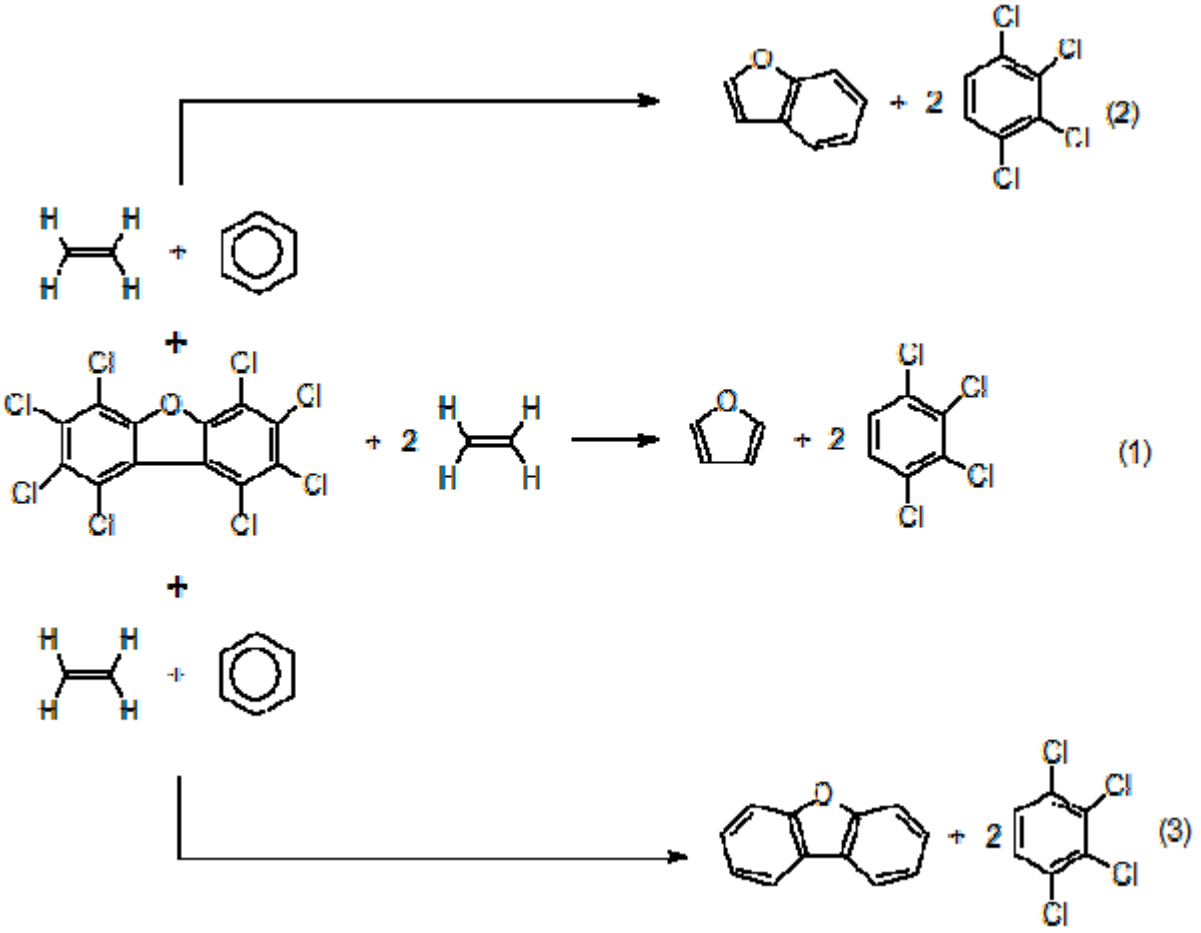
Chlorophenols



Chlorophenols

Molecule	Avg./3df*	PBEPBE/3d2f*	Exptal 1	Exptal 2	This work	Delta PBE
3mcp	-30,7	-30,9	-32,7	-31	-1,1	-1,0
4mcp	-30,3	-30,4	-30,6	-28,8	0,6	0,7
23dcp	-36,4	-36,5	-35		1,5	1,5
24dcp	-37,5	-37,7	-37,4	-35,5	1,0	1,2
25dcp	-38,5	-38,3	-37,9	-37	1,0	0,8
26dcp	-36,7	-36,4	-35	-34,1	2,1	1,9
34dcp	-34,7	-34,3	-35,9	-33,9	-0,3	-0,6
35dcp	-37,0	-36,5	-35,4	-33,9	2,3	1,9
penta	-45,5	-47,0	-48,8		-3,1	-1,8

Furans



Hepta/Octa Cl PCDF

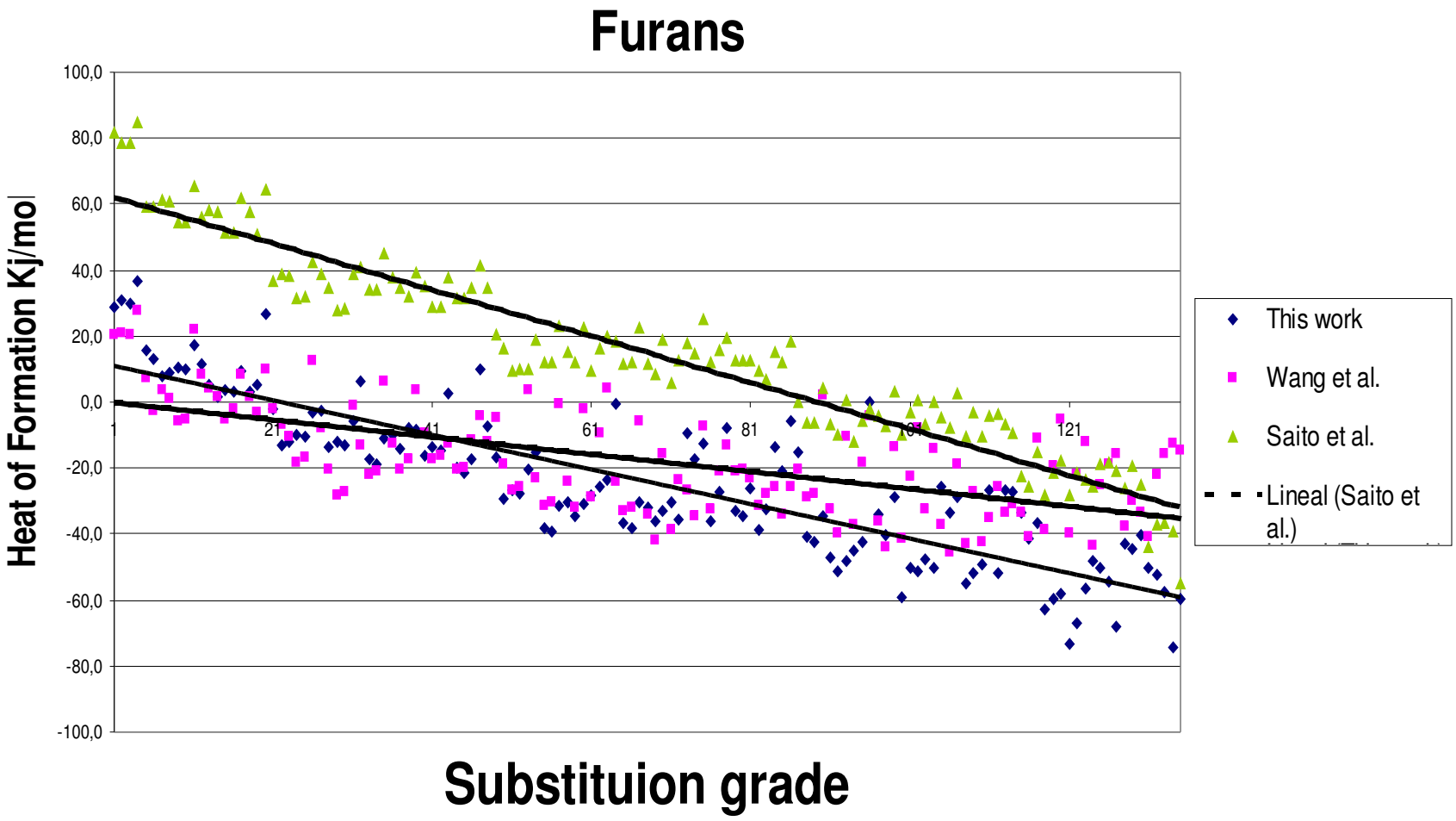
Table 4.3. PBEPBE/6-311+G(2df,2pd) calculations of the enthalpy of formation (in kJ mol^{-1}) of heptachloro and octachloro PCDFs.

Species	Reaction (1)	Reaction (2)	Reaction (3)	Mean Value	Wang[481]	Saito[475]
1234678-HpCDF	-48.3	-50.3	-52.7	-50.4	-40.6	-44.1
1234679-HpCDF	-50.2	-52.2	-54.6	-52.3	-21.8	-37.2
1234689-HpCDF	-55.6	-57.7	-60.0	-57.8	-15.8	-36.8
1234789-HpCDF	-72.3	-74.3	-76.7	-74.4	-12.8	-39.5
12346789-ODBF	-57.7	-59.7	-62.1	-59.8	-14.9	-55.1

Wang et al, Theochem,275,2005

Saito,Fuwa, Chemosphere,40,2000

Furans


Furans
100,0
80,0
60,0
40,0
20,0
0,0
-20,0
-40,0
-60,0
-80,0
-100,0
1
21
41
61
81
101
121
Heat of Formation Kj/mol
Substituion grade
This work
Wang et al.
Saito et al.
Lineal (Saito et al.)

Conclusion

- DFT is an appropiate tool in atmospheric thermochemistry
- Isodesmic reactions are suitable
- Non empirical PBE is the best
- Extensive basis set

Our team

- Prof. Dr. Oscar Ventura (Uruguay), leader
- Dr. María Paula Badenes (Argentina)
- Dr. Martina Kieninger (Uruguay)

Thank you, enjoy Santiago !!!