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Density Functional Theory Is More Accurate Than Coupled-Cluster Theory in the Study of the Thermochemistry of Species Containing the F−O Bond

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The standard singles and doubles coupled-cluster method including perturbational treatment of connected triple excitations, CCSD(T), and density functional methods, DFT, using a large, uncontracted, atomic natural orbital (ANO) basis set were employed for calculating the enthalpies of formation of some first-row atoms (H, N, O, F) as well as diatomic and triatomic molecules formed with them. Molecular enthalpies of formation at 298.15 K were obtained from enthalpies of reaction of the atoms, homonuclear diatomic molecules, and isodesmic reactions. It is shown that the errors are the minimum when isodesmic reactions are used. However, contrary to accepted belief, CCSD(T) gives a larger deviation from experiment than DFT in the latter case. DFT exhibits similar accuracy when using a very small basis set (6-31G*) to that with the extended basis set, while the errors obtained with CCSD(T) are much larger. It is concluded that DFT is a more accurate and convenient computational tool than CCSD(T) for the thermochemical study of species containing the F−O bond.

Introduction

Molecules containing fluorine−oxygen bonds represent a difficult subject for normally reliable ab initio methods.[1−7] These problems have been frequently addressed[7,8] by the use of singles and doubles plus perturbational triples coupled-cluster theory, CCSD(T).[9] Regretfully, the computational cost of such theory is so high that it can be applied routinely only to very small molecules.

The past years have witnessed a phenomenal increase in the application of density functional (DFT) methods to the study of chemical problems (see, for instance, refs 10−12). Both their increased speed over conventional ab initio methods and their accuracy are factors that have contributed to the popularity of DFT.

Different authors reported different degrees of success concerning DFT calculations on several F−O-containing compounds. Some authors concluded that DFT gives wrong results when applied to compounds containing these bonds.[5,13−16] Other authors, however, report surprisingly good results of DFT methods in the study of thermodynamics of reactions containing such compounds.[17,18] It has been suggested, on the basis of some of these calculations,[18] that the accepted enthalpy of formation of FOOF is wrong and should be revised.

Much of the confusion about whether DFT methods are appropriate for the description of fluorine−oxygen bonds arises from the different conditions under which calculations were performed. In fact, there are not systematic calculations in which DFT and CCSD(T) results obtained with the same, sufficiently large, basis set are compared among themselves for different compounds and properties. Therefore, we started a study in which we try to determine the accuracy of DFT methods in the calculation of thermochemical properties of molecules containing the F−O bond. This report contains the results obtained for the enthalpies of formation of first-row atoms and molecules, especially the compounds FO, FOH, FOF, and FOO. This paper reports on the first of a series of studies on the thermochemistry of molecules containing the F−O bond.

Theoretical Methods

A single, sufficiently large and flexible basis set was adopted for all the theoretical calculations in this study. The contracted atomic natural orbital (ANO) basis set of Widmarck, Malmqvist, and Roos[19,20] was selected but was used uncontracted to increase its flexibility. It is then a fully uncontracted (14s9p4d3f) basis set on first-row atoms and (8s4p3d) on H (polar five- and seven-component d- and f-polarization functions were used). This is the largest and most flexible basis set employed to perform geometry optimizations on the studied compounds that we are aware of. This basis set was systematically used for the calculation of optimum geometries, energies, properties, and evaluation of second derivatives for the calculation of vibrational frequencies.

CCSD(T)[9] calculations were performed correlating all the electrons (i.e., no frozen-core approximation). Geometry optimizations were performed using the Fletcher−Powell algorithm.[21] Second derivatives of the energy with respect to geometrical parameters were calculated numerically.

Density functional calculations were performed using two variants of the adiabatically connected functional of Becke,[22] B3LYP and B3PW91. B3LYP uses the exchange potential of Becke[23] plus a certain admixture of the exact Hartree−Fock exchange[22] and the correlation potential of Lee, Yang, and Parr

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TABLE 1: Enthalpies of Formation at 298.15 K of Some First-Row Atoms and Molecules Calculated with the Procedures Explained in the Text, Using the Large, Noncontracted Basis Set

		B3PW91			B3LYP			CCSD(T)		
	exp[d]	iso[e]	diat[f]	at[g]	iso[e]	diat[f]	at[g]	iso[e]	diat[f]	at[g]
H	52.10		70.99			51.24			50.63	
N	112.97		110.45			112.43			108.32	
O	59.56		60.68			59.99			56.22	
F	18.97		16.94			17.01			16.71	
rmse[b]			4.80			0.56			1.58	
max[c]			18.89			1.96			4.65	
HO	9.32	9.62	10.13	−9.59	8.87	9.46	10.74	7.36	7.95	13.04
		9.13			9.08			8.17		
NO	21.58		21.19	22.87		21.56	21.55		21.92	30.18
FO	26.05	25.75	24.93	26.12	26.50	24.31	26.13	28.01	26.42	32.30
		26.24			26.29			27.20		
HOH	−57.80	−58.10	−54.41	−93.30	−57.35	−54.07	−52.78	−55.84	−57.81	−51.54
FOH	−20.60	−20.30	−18.84	−36.83	−21.05	−19.20	−16.78	−22.56	−20.83	−12.64
		−20.41			−20.36			−19.45		
FOF	5.86	5.67	5.78	8.56	5.62	5.48	8.81	4.71	6.52	14.21
rmse[b]		0.09	0.68	7.25	0.13	0.73	1.18	0.55	0.27	2.88
max[c]		0.30	3.39	35.50	0.45	3.73	5.02	1.96	1.37	8.60

[a] In kcal/mol. [b] Root-mean-square error. [c] Maximum deviation from the experimental values. [d] Taken from the JANAF Thermochemical Data Tables; see text. [e] Using isodesmic reactions 1 (first entry) or 2 (second entry). [f] Using the reaction of formation from homonuclear diatomics. [g] Using the reactions of atomization.

(LYP).[24] B3PW91 replaces the LYP potential with that of Perdew and Wang.[25] Geometry optimizations were performed using internal coordinates and the default Berny optimization algorithm. Second derivatives were calculated analytically.

Very tight thresholds were used both for CCSD(T) and DFT geometry optimizations (1.5×10^{-5} and 6×10^{-5} au respectively for gradients and displacements). DFT and CCSD(T) calculations were performed with the Gaussian 94[26] code.

Standard statistical thermodynamics procedures were employed to calculate enthalpies of reaction, $\Delta_r H°(298.15)$, and formation $\Delta_f H°(198.15)$. The enthalpy of formation of the atoms H, N, O, and F were obtained as half the enthalpy of reaction for the atomization of the corresponding homonuclear diatomic molecule. Enthalpies of formation of the three diatomic radical oxides HO, NO, and FO as well as of the closed-shell triatomics HOH, FOH, and FOF were obtained by three different procedures. In the first place, the isodesmic reactions

$$\mathrm{FO} + \mathrm{HOH} \rightarrow \mathrm{FOH} + \mathrm{HO} + \Delta_r H°(1) \tag{1}$$

$$\mathrm{HO} + \mathrm{FOF} \rightarrow \mathrm{FOH} + \mathrm{FO} + \Delta_r H°(2) \tag{2}$$

were employed together with the experimental enthalpies of formation for three of the molecules involved to obtain the enthalpy of formation of the fourth. In the second procedure, the enthalpy of formation of the molecules was obtained calculating the $\Delta_r H°(298.5)$ of reactions involving the homonuclear diatomic molecules. For instance, the enthalpy of formation of NO was obtained as one-half the $\Delta_r H°(298.15)$ of the reaction

$$\mathrm{NO} + \mathrm{NO} \rightarrow \mathrm{N_2} + \mathrm{O_2} \tag{3}$$

No experimental value is involved in this way of calculating the enthalpies of formation, except for the definition of the enthalpies of formation of the elements in their natural state (i.e., the homonuclear diatomic molecules in the gaseous state at room temperature involved in these calculations) as zero. The third procedure employed for the calculation of the enthalpies of formation of the molecules resorts to the atomization reactions supplemented with the experimental enthalpies of formation of the atoms involved.

Two experiments were performed, besides the one described at length before, to assess the accuracy of the different procedures employed. A very small basis set, i.e., 6-31G*, was used to investigate the accuracy of the different procedures when less-than-optimal conditions must be used because of the size of the problem. Calculations using this basis set were performed at the CCSD(T), B3LYP, and B3PW91 levels. Several different isodesmic reactions were also employed to test whether the good agreement obtained with experiment when using reactions 1 and 2 were fortuitous or the result of deeper theoretical reasons.

Results and Discussion

Enthalpies of Formation Using a Large Basis Set. The most important results obtained are summarized in Table 1. Experimental values quoted in this table were obtained from the JANAF Thermochemical Tables.[27] The more recently recommended value given by Chase[28] was adopted for FO. In the case of FOH, the recommendations in the study of Pople and Curtiss[29] were followed. They showed that, according to the most recent determination of $\Delta_f H°(0)$ of $\mathrm{OH^+}$ by Katsumata and Lloyd,[30] the enthalpy of formation of FOH at 0 K should be −19.9 kcal/mol. Correcting it to 298.15 K gives an enthalpy of formation of −20.6 kcal/mol, the value adopted as experimental in this study. To facilitate the discussion, the enthalpies of formation of the atoms and those of the molecules are shown separately (Table 1).

Enthalpies of formation of the atoms calculated at the CCSD(T) level are quite mediocre, with minimum and maximum discrepancies with experiment of 1.5 and 4.7 kcal/mol. This was the expected behavior, since when using the atomization reactions for calculating the enthalpies of formation of the atoms there is no possibility of compensation of the errors inherent in the method. It is significant that the order of the error is $\mathrm{H_2} < \mathrm{F_2} < \mathrm{O_2} < \mathrm{N_2}$, implying that the error increases with the complexity of the bonding situation in the molecule.

B3LYP results in each of the four cases are closer to the experimental values than CCSD(T). Only in the case of fluorine is the error at this level larger than 1 kcal/mol. In this case there is no correlation between the magnitude of the error and the bonding complexity of the molecule. The other DFT method considered here, B3PW91, behaves intermediate between B3LYP and CCSD(T), except for hydrogen. It is obvious that there is a flaw in the B3PW91 combination of exchange and correlation potentials that results in an exceedingly small total energy for the H atom.

As stated before, three different methods were employed for calculating the enthalpies of formation of the molecules. The use of the isodesmic reactions, jointly with the experimental enthalpies of formation of three of the four species involved, gave the best results for DFT although not for CCSD(T). The $\Delta_r H^\circ(298.5)$ for reactions 1 and 2 is −20.47 and −9.73 kcal/mol experimentally (i.e., using the experimental enthalpies of formation of the four species to calculate the enthalpy of reaction). At the B3LYP and B3PW91 levels these values are −20.02 and −9.49 kcal/mol (B3LYP) and −20.77 and −9.54 kcal/mol (B3PW91)—in all cases less than 0.5 kcal/mol apart from the experimental value. At the CCSD(T) level instead, these enthalpies of reaction are −18.51 and −8.58 kcal/mol, respectively. Therefore, any enthalpy of formation obtained using these isodesmic reactions at the CCSD(T) levels will exhibit an error between 1 and 2 kcal/mol.

Thus, provided that the isodesmic reactions are used, B3PW91 (errors: 0.30 and 0.19 kcal/mol, respectively) is marginally better than B3LYP (errors: 0.45 and 0.24 kcal/mol), and DFT is better than CCSD(T), which exhibits errors of 1.96 and 1.12 kcal/mol. Nonetheless, the error is within so-called "chemical accuracy".

The second procedure, i.e., using the reactions of formation from the homonuclear diatomic molecules, gives worse results than with the isodesmic reactions for DFT, with maximum errors of up to 3.4 and 3.7 kcal/mol for B3PW91 and B3LYP, respectively. Contrary to accepted belief, CCSD(T) thermochemical results are better in this case than when using the isodesmic reactions. In fact, the maximum error here (for the HO molecule) is only 1.4 kcal/mol (half that of DFT). Furthermore, the enthalpies of formation of the other four molecules are within 0.4 kcal/mol of the experimental values, and the agreement with experiment is better for the larger molecules than for the smaller ones. An interesting point to note is that this method is purely theoretical and requires much less effort than using isodesmic reactions, since the homonuclear diatomics are calculated only once for each basis set used.

Finally, the third column reports the results obtained with each method when using the atomization reactions plus the experimental enthalpy of formation of the atoms. In this case, B3PW91 again exhibits behavior reported, whenever the H atom is involved (HO, H_2O, and FOH). It is interesting to notice that the error in the calculated value with respect to experiment *per H atom* is almost constant and can be written as 18 ± 2 kcal/mol. B3LYP behaves much more reasonably than B3PW91, but again the results are worse than with either of the other two procedures. CCSD(T) again behaves worse than B3LYP, but this time better than B3PW91 because of the already mentioned problem with the H atom.

In conclusion, from this experiment one can say that DFT performs better than CCSD(T) if the isodesmic reactions are used; however, CCSD(T) behaves better if the reactions of formation from the homonuclear diatomics are employed. Taking into account the enormous amount of time consumed by the CCSD(T) calculations with an extended basis set, B3PW91 calculations using isodesmic reactions seem to be the method to be preferred for this kind of study. However, employing DFT with the isodesmic reactions or CCSD(T) with the reactions of formation from the homonuclear diatomics are equivalent methods from the point of view of accuracy.

TABLE 2: Enthalpies of Formation at 298.15 K of Some of the Molecules in Table 1, Calculated with the Procedures Explained in the Text and the 6-31G* Basis Set[a]

		B3PW91		B3LYP		CCSD(T)	
	exp	iso	diat	iso	diat	iso	diat
HO	9.32	8.93	16.10	8.33	17.13	5.09	13.30
FO	26.05	26.44	23.08	27.04	24.53	30.28	26.24
HOH	−57.80	−57.41	−42.74	−56.81	−41.39	−53.57	−42.34
FOH	−20.60	−20.99	−13.60	−21.59	−13.47	−24.83	−13.16
rmse		0.20	4.55	0.50	4.90	2.12	4.40
max		0.39	15.06	0.99	16.41	4.23	15.46

[a] See footnotes to Table 1.

The Use of a Small Basis Set. Given the conclusions of the previous section, it is interesting to investigate whether they are also valid in the limit of small basis sets, which have to be used for the study of larger species than those considered here. Table 2 reports the enthalpies of formation obtained at the B3PW91, B3LYP, and CCSD(T) levels with the 6-31G* basis set.

It can be observed in this case that the calculation of enthalpies of formation with respect to the homonuclear diatomics gives very poor results. The errors are particularly large for water and FOH, and both DFT and CCSD(T) behave equally wrong. This is not true however with respect to the enthalpies of formation calculated from the isodesmic reaction 1. In this case, DFT (particularly B3PW91) gives results practically as good as those obtained with the much larger uncontracted basis set, with a maximum error of 0.39 kcal/mol. CCSD(T) does not behave so well, showing an error 2 times larger than with the extended basis set. Although the error is not within chemical accuracy, it is anyway quite remarkable that one can get results so close to experiment with such a small basis set. The results are, of course, connected with how well each method reproduces the enthalpy of reaction 1. Values of −10.08, −19.48, and −16.24 kcal/mol were obtained respectively for B3PW91, B3LYP, and CCSD(T) with the 6-31G* basis set, to be compared with the experimental −10.47 kcal/mol, or those obtained with the larger basis set, −20.77, −10.02, and −18.51 kcal/mol, respectively.

The conclusion of this experiment is that B3PW91 with the very small 6-31G* basis set and the isodesmic reaction gives results that are as good as those obtained at the same level with the larger basis set and better than CCSD(T) using either the small or extended basis sets.

Other Isodesmic Reactions. It is clear from the results in the previous sections that the use of the isodesmic reactions at the DFT level gives very accurate results. However, it is valid to question whether this was just a casual agreement. An attempt to answer this question was done performing only DFT geometry optimizations and thermochemical calculations of some other molecules (FOF, FOO, and HOO), exploring then other isodesmic reactions. The enthalpies of reaction for the species studied are collected in Table 3. The complete study of these reactions employing CCSD(T) will be published elsewhere.

It is clear from the six reactions presented that both B3PW91 and B3LYP estimated $\Delta_r H^\circ(298.5)$ are very near to the experimental value (maximum deviation is 1.2 kcal/mol in both cases). From each one of these reactions it is possible to obtain the enthalpy of formation of at least one of the interesting species containing the F−O bond, and we present these results in Table 4. Averaging the enthalpies of formation of each compound

TABLE 3: Enthalpies of Reaction at 298.15 K of Several Isodesmic Reactions Involving Species Containing the F−O Bond[a]

		enthalpy of reaction		
	reaction	exp[b]	B3PW91	B3LYP
I	FOH + OH → FO + HOH	−20.47	−20.76	−20.06
II	FOF + OH → FO + FOH	−9.73	−9.54	−9.50
III	FOO + OH → FO + HOO	11.16	12.19	12.32
IV	FOO + OH → OO + FOH	−35.99	−35.63	−34.78
V	FOH + FOO → FOF + HOO	20.89	21.60	21.82
VI	FO + HOH → FOH + HOO	31.63	32.82	32.37
rmse[c]			0.30	0.35
max[c]			1.19	1.21

[a] In kcal/mol. [b] Obtained using the experimental enthalpies of formation at 298.15 K. [c] See footnotes to Table 1.

obtained from the different reactions, we get the results shown in the last column of Table 4.

The main conclusion to be obtained from Table 4 is that all the calculated enthalpies of formation are within chemical accuracy. In no case is there any deviation larger than 1.3 kcal/mol, and in most cases it is smaller than 1 kcal/mol. Taking 2 times the standard deviation as a measure of the dispersion of the values, it can be concluded from Table 4 that the precision and accuracy with which enthalpies of formation can be calculated by this method are better than 1.0 kcal/mol for all the molecules containing the F−O bond.

Strength of the O−H and F−O Bonds. With the data obtained one can also compare how well the different methods describe the weakening of the O−H bond in FOH compared to HOH and the corresponding strengthening of the F−O bond in FOH compared to FOF. Experimentally, the bond dissociation energy of the O−H bond in water is 119 ± 1 kcal/mol,[31] while that of the F−O bond in FOH and FOF are 47.5 [29] and 40 ± 1 kcal/mol,[32] respectively. We are not aware of any experimental data for the strength of the O−H bond in FOH. Therefore, we preferred to compare the $\Delta_r H°(298.5)$ for the reactions of dissociation XOY → XO + Y. In this way we can use the experimental enthalpies of formation to obtain experimental enthalpies of reaction in the four cases. The results obtained with DFT and CCSD(T) calculations using the extended basis set are collected in Table 5.

One can see that for these reactions, which are not isodesmic, CCSD(T) calculations are invariably closer to the experimental results than DFT. Leaving aside the case of B3PW91 for the O−H bond (because of the flaw pointed out before), one sees that the DFT error lies in the interval 3−5 kcal/mol, while the CCSD(T) error is lower, in the interval 1−4 kcal/mol. Comparing the three methodologies, one sees that the calculations predict a weakening of the HO bond in FOH, as compared to HOH, of about 18−20 kcal/mol, while the strengthening of the F−O bond in FOH with respect to FOF is lower, of about 9 kcal/mol.

Conclusions

Enthalpies of formation of several first-row atoms as well as diatomic and triatomic molecules formed with them were calculated employing density functional and coupled-cluster methods using a large, uncontracted, spdf basis set on one side and the small 6-31G* basis set on the other. Geometry optimizations were performed at the same level at which energies were calculated, and no frozen-core approximation was employed for the CCSD(T) calculations. Enthalpies of formation were calculated using isodesmic reactions, with respect to reactions of homonuclear diatomic molecules and reactions of the atoms (using the enthalpies of atomization and the experimental enthalpies of formation of the atoms).

It was shown that DFT, when coupled with a convenient isodesmic reaction for the species of interest, can produce enthalpies of formation that are in excellent agreement with experiment. This conclusion seems to be independent of the basis set used. Furthermore, this conclusion is essentially independent of the isodesmic reaction chosen. The enthalpies of reaction calculated for several isodesmic reactions exhibit errors below 1.2 kcal/mol with respect to experiment and are within the experimental error bars. Enthalpies of formation of the molecules containing the F−O bond show agreement with experiment at the level of 1.0 kcal/mol or better.

It was also shown here that the purely theoretical procedure of calculating the enthalpies of formation from the reactions of homonuclear diatomic molecules exhibits larger errors than the previous procedure for DFT. Although larger than what is usually called "chemical accuracy", the errors are still not unreasonable (under 4.0 kcal/mol) when the large basis set was used. However, the method failed when the small basis set was employed, and maximum errors of up to 16 kcal/mol were found.

The method of using the enthalpies of atomization plus the experimental enthalpy of formation of the atoms was shown to be the worst procedure. For B3LYP and CCSD(T) the maximum errors were over 5.0 and 8.0 kcal/mol, respectively. For B3PW91 the procedure turned out to be totally unacceptable, because the error connected to the total energy of the H atom spoiled completely the calculation of enthalpies of formation of any molecule containing hydrogen (HO, FOH, etc.).

Finally, it was shown that, contrary to accepted belief, CCSD(T) employing a large basis set and with no approximations involved is worse than DFT when employing the procedure

TABLE 4: Enthalpies of Formation at 298.15 K of Molecules Containing the F-O Bond, Calculated from the Reactions in Table 3[a]

species	method	I	II	III	IV	V	VI	average[b]
FO	B3LYP	26.46	26.28	27.21	00.00	00.00	00.00	26.65 ± 0.60
	B3PW91	25.76	26.24	27.08				26.36 ± 1.86
	Exp.							26.05 ± 2.4
FOH	B3LYP	−21.01	−20.37		−19.39	−21.53	−19.86	−20.43 ± 1.92
	B3PW91	−20.31	−20.41		−20.24	−21.31	−19.41	−20.35 ± 1.34
	exp							−20.60 ± 1.0
FOF	B3LYP		5.63			6.79		6.21 ± 1.64
	B3PW91		5.67			6.57		6.12 ± 1.28
	exp							5.86 ± 0.5
FOO	B3LYP			4.91	4.86	5.14	5.33	5.06 ± 0.50
	B3PW91			5.04	5.71	5.36	4.88	5.48 ± 0.42
	exp							6.07 ± 0.5

[a] In kcal/mol. [b] Arithmetic mean plus 2 times the standard deviation.

TABLE 5: Strength of the O−H and F−O bonds in HOH and FOH, According to the Different Computational Methods Used in This Paper[a]

method	H−OH	H−OF	F−OH	F−OF
B3LYP	115.05	95.00	45.91	36.42
B3PW91	135.81	115.05	46.20	36.66
CCSD(T)	116.68	98.17	45.77	37.19
exp[b]	119.22	98.70	48.89	39.11

[a] Absolute values of the enthalpies for the reaction XOY → X + OY are given; in kcal/mol. [b] Experimental values obtained from the enthalpies of formation.

relying on the isodesmic reactions. When using the reactions of the homonuclear diatomic molecules with the large basis set, CCSD(T) was able to give almost perfect results for NO, FO, HOH, and FOH, although it gave a larger error for HO and FOF. The procedure did not hold up when the small basis set was employed, and errors of up to 15 kcal/mol were found (the same as with DFT).

All in all, it can be said that density functional theory is better than CCSD(T) in the task of evaluating enthalpies of reaction of isodesmic reactions and using them to calculate enthalpies of formation of the molecules containing the F−O bond. The fact that practically the same result can be obtained with a large and a small basis set gives even more support to this assertion. If isodesmic reactions can be written for the compound to be investigated, and reliable experimental or theoretical enthalpies of formation do exist for the rest of the compounds involved, this procedure gives a very fast way of estimating reliable enthalpies of formation. If no isodesmic reaction can be built with the existing data, then one can resort to the DFT evaluation of the enthalpy of the reaction of the homonuclear diatomic molecules (if possible) and obtain a result within 4 or 5 kcal/mol of the experimental one. If better accuracy is necessary, then the CCSD(T) calculation of the enthalpies of formation using the homonuclear diatomic molecules is recommended. In this case one should expect an error below 0.5 kcal/mol.

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