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ARTICLE TYPE

Accurate Predictions of C-SO₂R Bond Dissociation Enthalpies with Density Functional Theory Methods

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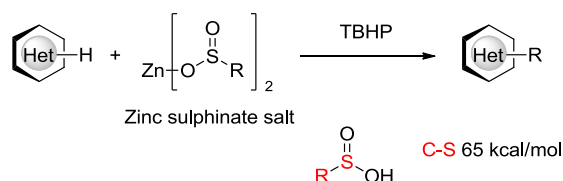
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The dissociation of C-SO₂R bond frequently involves in organic and bio-organic reactions, and the C-SO₂R bond dissociation enthalpies (BDEs) are potentially important for understanding the related mechanisms. The primary goal of the present study is to provide a reliable calculation method to predict the different C-SO₂R bond dissociation enthalpies (BDEs). Comparing the accuracies of 13 different density functional theory (DFT) methods (such as B3LYP, TPSS, and M05 etc), and different basis sets (such as 6-31G(d) and 6-311++G(2df,2p)), we found that M06-2X/6-31G(d) gives the best performance in reproducing the various C-S BDEs (and especially the C-SO₂R BDEs). As an example for understanding the mechanisms with the aid of C-SO₂R BDEs, some primary mechanistic studies were carried out on the chemoselective coupling (in the presence of Cu-catalyst) or desulfurative coupling reactions (in the presence of Pd-catalyst) between sulfinic acid salts and boryl/sulfinic acid salts.

1. Introduction

Sulfinic acid and its salts have been frequently used in organic and bioorganic synthesis,¹⁻⁶ and have shown great potential in preparing biologically active compounds (such as sulphone^{3,4}). For example, Fujiwara et al. recently reported C-H functionalization of heterocycles activated by the zinc sulphinate salts (Scheme 1),⁵ representing novel, highly efficient and easily accessible strategies for synthesis of various motifs in pharmaceutical chemistry. Analyzing the reaction mechanism, Fujiwara et al. proposed that the facile homolytic dissociation of the C-SO₂R bond (relative to C-CO₂R and C-B(OR)₂ bonds) is important for the overall reaction efficiency. Similarly, the C-SO₂R bond dissociation has also been found to be involved in many other organic and bioorganic reactions (such as the recently developed desulfurative coupling reactions⁶), where the C-SO₂R bond strength is determinant for the overall reaction rates.⁷ Accordingly, the evaluation of C-SO₂R bond dissociation energies/enthalpies (BDEs) will aid the mechanistic understandings on the extensively reported C-SO₂R involving reactions, and also benefit the design of novel synthetic reactions.



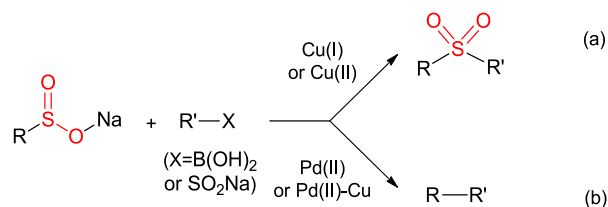
Scheme 1. Zinc sulphinate salts activated C-H functionalization of heterocycles reported by Fujiwara et al.

Due to the experimental difficulties,⁸ the C-SO₂R BDEs have

been rarely reported (less than 10 to the best of our knowledge). For example, Horowitz evaluated the bond dissociation enthalpies of MeSO₂• via complex kinetic studies of the radiolysis of MeSO₂Cl in cyclohexane,¹¹ and Cornell conducted toluene carrier studies on the pyrolysis of trimethylene sulfone and 2-methylsulfolane to determine the related C-SO₂R bond strengths.¹² In the present study, we attempt to find out an alternative to evaluate the C-SO₂R BDEs with the aid of DFT calculations. Similar to the previous studies on calculations of BDEs of organic compounds,^{9,10} the experimentally measured BDEs of several C-SO₂R compounds were first chosen as the benchmarking samples. Meanwhile, considering that the C-SO₂R BDEs are too scarce to evaluate the accuracy of different calculation methods, we also selected 21 other structurally representative C-S compounds (including alkyl/aryl thioles, sulfide, and disulfide)¹³ as the test samples to find out a generally-applicable method in treating different types of C-S BDEs.

Efforts were first made to compare the accuracy of different calculation methods. The performance of 13 different DFT functionals (such as B3LYP,¹⁴ BB1K,¹⁵ and M05¹⁶ etc) and 6 different total electron basis sets (such as 6-31G(d), and 6-31+G(d) etc) have been examined. Similar to Truhlar's previous proposals,¹⁷ M05-2X,¹⁸ M06,¹⁹ and M06-2X²⁰ are found to be accurate in reproducing the reported C-S BDEs. In contrast, the performance of several other methods, including BB1K, MPW1K,²⁰ MPW3LYP,²¹ MPWB1K,²² PBE,²³ TPSS,²⁴ TPSSLYP1W²⁵, are much worse. All these methods were suggested to be used with caution in treating the reaction systems involving the C-S bond dissociation processes.²⁶ In addition, the overall performance of M06-2X/6-31G(d) is found to be the best after examining the basis set effect. On this basis, some preliminary mechanistic understandings on the fascinating

chemoselective reactions between the sulfinic acid salts and boryl/sulfinic acid salts (the Cu-catalyzed couplings⁴ in Scheme 2a and the Pd or Pd/Cu catalyzed desulfurative couplings⁶ in Scheme 2b) have been provided. We wish our calculation method and analysis will be helpful for future mechanistic study and the development of more efficient C-SO₂R involving reactions.



Scheme 2. Cu- or Pd- (Pd/Cu-) catalyzed coupling or desulfurative couplings between sulfinic acid salts and boryl/sulfinic acid salts.

2. Results and Discussion

2.1 Calculation of C-S BDEs

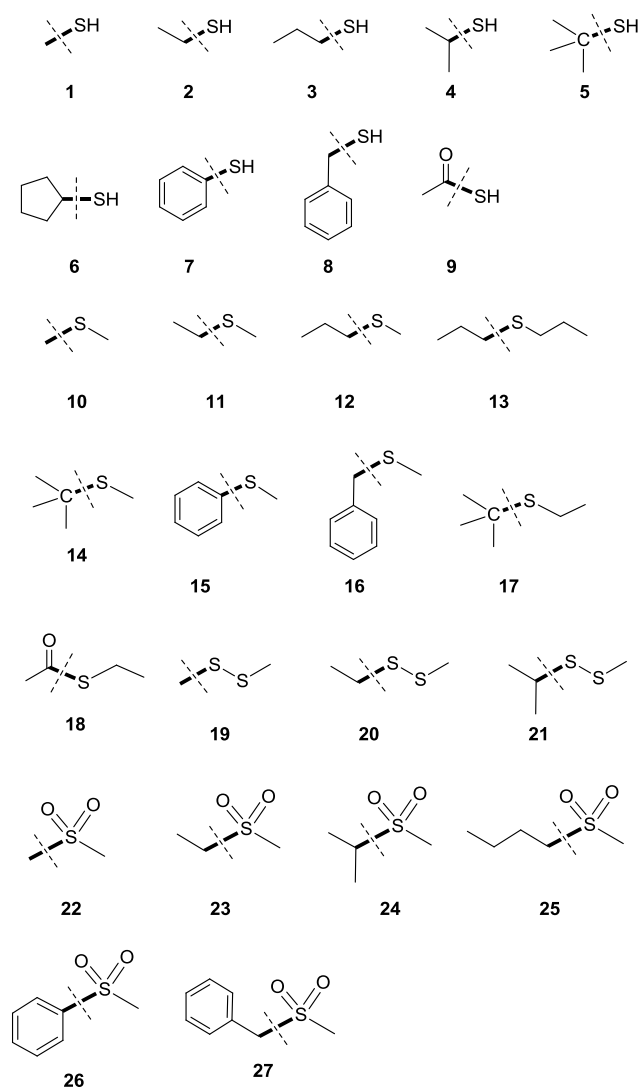


Figure 1. The selected C-S compounds for evaluation of different theoretical methods.

As mentioned in the introduction, several structurally representative C-S compounds (**1-27**, Figure 1) have been selected as samples to evaluate the accuracy of different calculation methods.

Similar to the previous theoretical studies in predicting the BDEs of organic and organometallic compounds,^{9,10} the linear correlation factor (the linear correlation coefficient *R* and the square deviation *SD*) together with the room-mean-square-deviation (RMSD) between the calculation results and the experimental ones are used to evaluate the accuracy of different methods. The performance of 13 different functionals (including B3LYP, BB1K, M05, M05-2X, M06, M06-2X, M06-L,²⁷ MPW3LYP, MPWB1K, PBE, TPSS, and TPSSLYP1W) has been first examined (with 6-31G(d) basis set). The detailed calculation results and the linear correlations between the calculation and experimental results are given in Table 1.

Table 1. Comparison between BDEs calculated by *DFT*/6-31G(d) and the experimental results of the selected C-S compounds in Figure 1.^{a-c}

Reactant	BDE ^{exp}	BDE ^{calc}		
		B3LYP	BB1K	M05
1	74.7±1	70.5	79.0	73.9
2	73.6±0.5	67.7	75.2	70.7
3	74.2±0.7	68.0	75.4	71.1
4	73.4±0.9	65.4	72.5	67.9
5	72.0±0.9	62.1	68.9	64.3
6	71.0±1.2	63.3	69.9	65.8
7	86.2±1.5	80.5	87.1	83.2
8	61.7±1.5	54.5	61.8	56.8
9	73.6±1.5	69.3	75.6	75.0
10	73.6±0.8	66.7	74.8	71.3
11	72.4±1	63.8	70.9	68.1
12	73.3±1.5	64.0	70.9	68.2
13	72.8±1.5	64.0	70.9	67.1
14	70.4±1.5	56.6	62.5	60.4
15	85.4±1.5	76.4	82.9	80.4
16	60.5±1	51.3	57.9	55.2
17	71.1±1.5	56.6	62.1	59.1
18	76.2±2	68.2	73.2	73.9
19	57.4±1.5	53.3	52.2	57.2
20	56.2±2	50.7	54.3	54.0
21	54.5±2	48.2	51.5	51.2
22	68	59.3	61.7	66.7
23	68.9±2	57.2	58.7	64.2
24	67.5±2	54.5	55.6	60.9
25	71.3±2	57.4	59.4	63.9
26	82.3±2	68.3	68.7	74.4
27	57.5±2	43.7	45.0	50.0

R	/	0.9158	0.7929	0.9329	7	85.2	82.2	89.1	86.9
SD(kcal/mol)	/	3.3	5.1	3.0	8	60.1	56.3	63.5	60.9
RMSD(kcal/mol)	/	9.4	6.2	5.5	9	74.9	71.1	77.5	77.6
BDE ^{calc}									
Reactant	M05-2X	M06	M06-2X	M06-L	11	68.6	66.0	73.0	70.0
1	76.7	74.9	76.9	74.1	12	68.7	66.0	72.9	70.1
2	75.0	72.8	75.5	71.9	13	68.9	65.2	72.9	69.9
3	75.5	73.3	75.2	72.4	14	61.3	57.2	65.0	63.0
4	74.0	71.7	74.4	70.0	15	81.2	78.9	85.1	82.6
5	73.7	69.9	73.7	67.2	16	56.6	53.9	60.0	57.7
6	71.5	69.1	72.0	67.7	17	60.3	56.5	64.6	62.8
7	87.7	84.6	86.9	84.0	18	72.8	69.4	75.2	75.7
8	61.8	60.0	63.6	59.1	19	56.8	53.8	60.2	57.9
9	75.7	76.5	76.2	76.1	20	53.9	50.8	56.2	55.0
10	72.5	72.8	75.2	70.0	21	51.4	47.6	54.3	52.8
11	71.1	70.2	74.2	68.0	22	60.7	56.8	63.9	62.4
12	71.1	70.9	74.0	68.1	23	58.3	54.6	61.2	60.2
13	71.9	70.2	73.0	67.8	24	55.3	51.1	58.4	57.5
14	69.0	67.5	71.7	62.8	25	58.9	54.0	61.8	60.3
15	84.9	82.3	86.0	80.0	26	69.1	65.1	71.3	70.4
16	60.2	59.5	64.6	56.7	27	45.5	41.6	47.5	46.7
17	69.5	66.1	70.4	62.5					
18	74.9	75.6	76.1	75.8	R	0.8451	0.8086	0.8097	0.8449
19	59.9	59.3	61.3	55.8	SD(kcal/mol)	4.4	4.9	4.9	4.4
20	58.6	56.8	60.1	54.9	RMSD(kcal/mol)	6.5	9.6	4.9	5.3
21	58.3	56.4	59.8	52.3					
22	69.3	67.6	69.4	63.0	BDE ^{calc}				
23	69.0	66.2	69.4	61.9	Reactant	TPSS	TPSS		
24	68.8	65.6	69.1	60.0			LYP1W		
25	68.9	67.1	69.8	62.3	1	71.9	69.0		
26	80.7	76.8	79.8	71.3	2	69.2	66.5		
27	56.2	53.8	58.1	49.1	3	69.5	66.7		
					4	67.3	64.6		
R	0.9794	0.9700	0.9784	0.9237	5	64.2	61.4		
SD(kcal/mol)	1.7	2.0	1.7	3.2	6	65.0	62.8		
RMSD(kcal/mol)	1.6	2.5	2.1	5.2	7	81.6	78.8		
					8	56.3	53.0		
					9	72.1	68.6		
					10	68.6	65.8		
					11	65.8	63.2		
					12	66.0	63.2		
					13	65.1	62.6		
					14	59.3	56.7		
					15	78.1	75.4		
					16	53.9	50.4		
</									

17	58.4	56.7
18	70.4	67.6
19	53.2	50.9
20	50.8	48.6
21	48.7	46.5
22	56.0	52.4
23	54.3	50.9
24	51.9	48.8
25	54.5	51.0
26	64.8	61.9
27	41.2	37.5
<hr/>		
R	0.8259	0.8111
SD(kcal/mol)	4.6	4.8
RMSD(kcal/mol)	5.4	12.0

^a The regression slopes for all correlations of calculation and experimental results are fixed at 1.00.

^b The data are cited from ref 28.

^c R: linear correlation coefficient ; SD (standard deviation) = $\left[\sum (x_i - \bar{x})^2 / (N-1) \right]^{1/2}$ (N=30, $i=1-30$, x_i represents the calculated data

for each species, \bar{x} is the mean of the 16 calculated data); RMSD (root-mean-square deviation) = $\left[\sum (x_i - y_i)^2 / N \right]^{1/2}$ (N=30, x_i represents the calculated data for each species, and y_i represents the experimental data accordingly)

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According to the calculation results in Table 1, the accuracy of different methods varies much for predicting the concerned C-S BDEs. First, the performance of M05-2X, M06, and M06-2X functionals are significantly better than those of the other methods, reflecting from the relatively higher linear fit coefficient ($R > 0.97$) and the lower deviation values ($SD < 2$ kcal/mol; $RMSD < 2.5$ kcal/mol). Second, the linear correlations between the calculation results with M05, M06-L and B3LYP methods are slightly worse than the aforementioned three methods ($0.9 < R < 0.95$, $SD \sim 3.0$ kcal/mol), whereas the RMSD values are relatively large (cal. 5 kcal/mol). Third, the accuracy of the other methods (including BB1K, MPW1K, MPW3LYP, MPWB1K, PBE, TPSS, TPSSLYP1W) are all quite poor ($R < 0.9$, and $SD/RMSD > 4.5$ kcal/mol), and in some cases the deviation between the calculated BDEs and the experimentally measured ones are even over 20 kcal/mol (e.g. TPSSLYP1W for **26**: **MeSO₂-Ph**). The observation that BB1K, MPW1K, MPW3LYP, and MPWB1K etc tend to systematically underestimates the BDE of organic compounds have also been found in many of the previous publications.²⁶ Therefore, we suggest that these methods (M05, M06-L, B3LYP, BB1K, MPW1K, MPW3LYP, MPWB1K, PBE, TPSS, TPSSLYP1W) should be used with caution in treating the reaction systems involving the C-S bond dissociation processes.

More importantly, comparing the accuracy of M05-2X, M06 and M06-2X in treating the BDEs of C-SO₂R compounds (**22-27**), we found that the linear correlation coefficients between the calculation results and the experimental ones with M05-2X and M06-2X are both over 0.98 (Table 2), while the SD values are

both lower than 1.7 kcal/mol (Note: the error bar of the experimental data is generally 2 kcal/mol). The linear correlations of C-SO₂R BDEs with M06 method is slightly worse ($R=0.9756$, $SD=1.8$), and the RMSD value is 3.5 kcal/mol. Accordingly, both M05-2X and M06-2X are concluded to be more reliable in calculating the C-SOOR BDEs (than all the other concerned methods). For clarity reasons, the linear correlation plot between the calculation results (with M05-2X/6-31G(d) and M06-2X/6-31G(d) methods) are given in Figure 2.

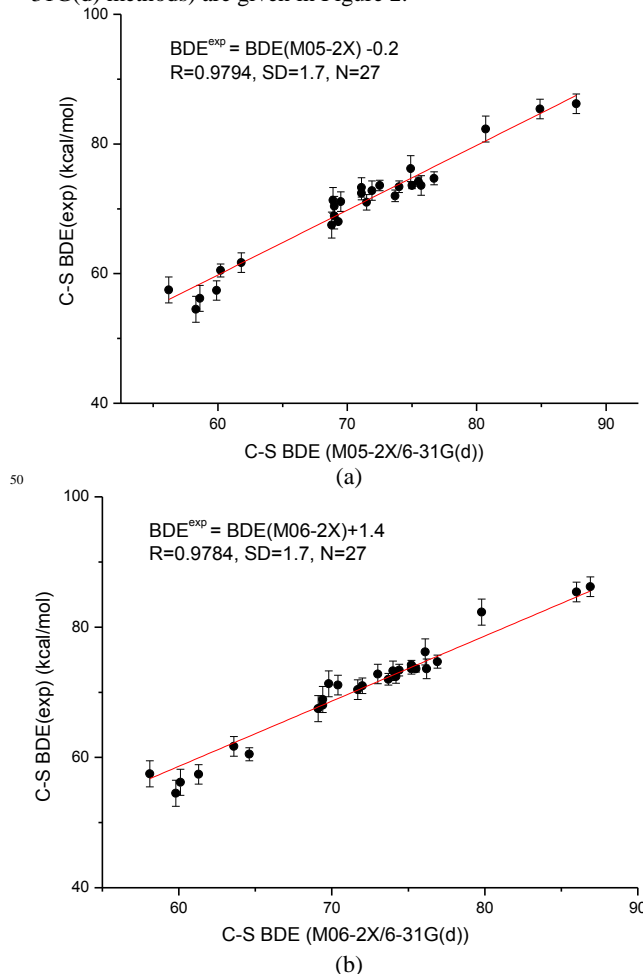


Figure 2. The correlations between the theoretical (by using left: M05-2X/6-31G(d) and M06-2X/6-31G(d)) and experimental C-S BDEs for complexes **1-27**.

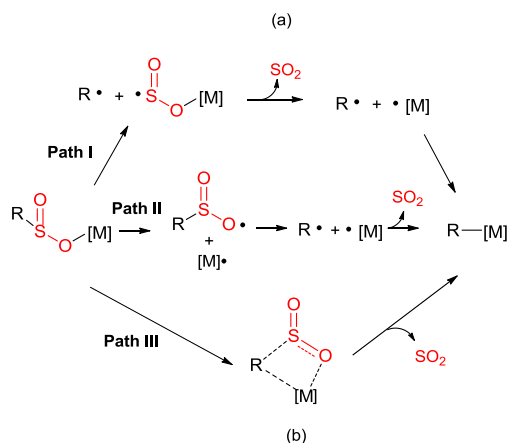
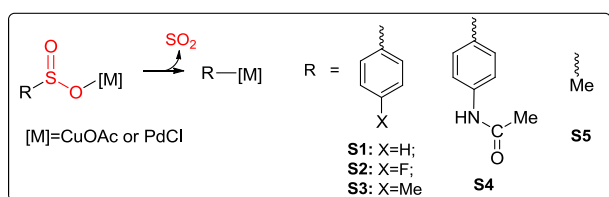
After obtaining the good functionals (M05-2X and M06-2X), we next examined the effect of different basis sets (i.e. 6-31G(d), 6-31+G(d), 6-31+G(d,p), 6-311+G(d,p), 6-311++G(d,p), 6-311++G(2df,2p)). The related calculation results indicate that the accuracy with different basis sets are all comparable ($R \sim 0.98$, $SD/RMSD \sim 2$ kcal/mol for all the compounds in Figure 1), unless the very time-consuming M06-2X/6-311++G(2df,2p) method ($R = 0.9878$, $SD = RMSD = 1.3$ kcal/mol) (For clarity reasons, the detailed calculation results have been provided in the supporting information). The results suggest that the utilization of higher basis sets does not always lead to higher accuracy. Finally, considering that M06-2X/6-31G(d) is relatively less time-consuming (relative to the M06-2X/6-311++G(2df,2p)), and gives the best R value for the concerned C-SOOR compounds,

we use this method for the following calculations and discussions.

2.2 Preliminary mechanistic understanding on the chemoselectivity of coupling or desulfative coupling reactions.

As mentioned in the introduction, the σ C-SOOR bond strength might be potentially helpful for understanding the reaction mechanisms. In the present study, the mechanism of the intriguing Cu- or Pd-catalyzed chemoselective coupling or desulfative coupling reactions has been chosen as examples. A similar analysis has been performed previously for the related decarboxylative coupling reactions.^{30,31}

Considering that the concerned two reaction systems are mainly differentiated by whether SO_2 is released or not, we mainly focus on the desulfative elementary step (Scheme 3a). Several experimentally used,^{4,6} structurally representative disulfide compounds (**S1-S5**) were chosen as the substrates, and three main mechanistic possibilities have been examined (Scheme 3b). In Path I, the C-SOO[M] bond dissociation occurs first, following with the dissociation of SO_2 from the $\bullet\text{SO}_2[\text{M}]$ and the bond formation between $\text{R}\cdot$ and $\bullet[\text{M}]$. In Path II, the $\text{RSO}_2\text{-M}$ bond dissociation occurs prior to the dissociation of SO_2 from the formed $\text{R-SO}_2\cdot$. In Path III, a concerted SO_2 dissociation occurs via the four-membered transition state, from which the release of SO_2 occurs to generate R-[M] .



Scheme 3. The concerned desulfative step (a) and the mechanistic possibilities (b).

According to the calculation results (Table 2), the possibility of Path I can be easily excluded because the C-SOO[M] ($[\text{M}] = \text{PdCl}$ or CuOAc) bond cleavage is very energy demanding (BDE > 60 kcal/mol for all concerned systems). Interestingly, examining the energy demands of Path II, we found that the $\text{RSO}_2\text{-Cu(OAc)}$ bond dissociation is highly disfavored (BDE > 105 kcal/mol), whereas the $\text{RSO}_2\text{-PdCl}$ bond dissociation is fairly feasible (BDE ~ 28 kcal/mol for the aryl substituted compounds and ~32 kcal/mol for the alkyl substituted compounds). The observation is expected because the relatively smaller atom

radius of Cu leads to stronger interactions between the metal center and the $-\text{SO}_2\text{R}$ group. Meanwhile, it's noteworthy that the energy demands of the $\text{RSO}_2\text{-PdCl}$ are modest, and can be possibly achieved under the experimental conditions (r.t.-60°C). Therefore, the subsequent steps in Path II were further examined. As shown in Table 2, the energy demand of the C-SOO \bullet bond dissociation is also modest (about 32 kcal/mol for the aryl substituents and 20 kcal/mol for alkyl substituent). In this context, we concluded that the overall energy demands for the concerned complexes in the Pd-catalyzed systems are all around 32 kcal/mol. Meanwhile, examining the energy demands of Path III, we found that the energetics in Pd- and Cu- systems are also distinct. The activation barriers of the desulfative step in the Pd-systems are all quite facile (barrier < 21 kcal/mol for all concerned species), whereas the energy barriers of the desulfative step in the Cu-systems are significantly higher (> 35 kcal/mol).

Table 2. The energy demands of different mechanisms (in kcal/mol).

		Path I	Path II	
	Reactant	BDE(C-SOO[M])	BDE(CSOO-[M])	BDE(C-SOO•)
[M] = ClPd-	S1	65.4	28.6	31.7
	S2	65.5	28.4	32.0
	S3	65.9	28.3	32.5
	S4	66.3	28.0	33.2
	S5	57.7	32.1	20.6
[M] = (OAc)Cu-	S1	93.8	108.6	31.7
	S2	94.3	108.8	32.0
	S3	94.4	108.4	32.5
	S4	95.6	108.8	33.2
	S5	84.0	110.0	20.6

	Reactant	Path III	BDE(C-[M])
		ΔH^\ddagger	
[M] = ClPd-	S1	11.1	55.7
	S2	11.3	55.3
	S3	10.5	56.0
	S4	10.5	55.4
	S5	20.3	46.3
[M] = (OAc)Cu-	S1	38.9	76.6
	S2	37.5	76.2
	S3	38.4	75.9
	S4	38.2	75.5
	S5	44.4	65.8

Comparing the relative facility of Path I-III, we found that Path III is the most favorable mechanism for both the Pd- and Cu-catalyzed systems. The phenomenon is understandable, because the steric effect in the concerned systems is negligible, and thus the endothermic C-SOO[M] or CSOO-[M] bond dissociations can be greatly compensated by the exothermic C-[M] bond formation process (for clarity reasons, the BDEs of C-[M] bonds are also given in Table 2). Meanwhile, all the concerned BDEs (C-SOO[M], CSOO-[M] or C-[M]) in the Cu-catalyzed systems (entries 6-10) are higher than the related ones in the Pd-catalyzed systems, and the reason might be related to that the more diffuse 4d orbital of Pd (relative to the 3d orbital of Cu) weakens the related chemical bond.³² More importantly, considering that the strengthened C-SOO[M] and C-[M] bond in Cu-systems (relative

to the related Pd-systems) might be counteracted in some extent, we conclude that the main contribution of the difficulty in desulfinitative step in Cu-systems lie in the significantly stronger RSOO-[Cu] bond. Note that the relative energy demands in different reaction systems also corroborate the previous experimental observations that the sulfinic group tends to be retained in the Cu-catalyzed reaction systems ($\Delta H^\ddagger > 35$ kcal/mol, entries 6-10 in Table 2),⁴ while the desulfinitative coupling is feasible under the Pd-catalyzed reaction systems ($\Delta H^\ddagger < 21$ kcal/mol, entries 1-5).⁶

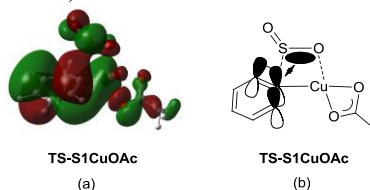


Figure 3. HOMO of TS-S1CuOAc (a) and an illustrative figure (b).

Finally, it's noted that in the Pd-systems, the activation barriers of the different aryl complexes are all comparable (entries 1-4, ~10 kcal/mol), whereas the barrier of the alkyl system is relatively higher (entry 5, cal. 20 kcal/mol). Similar observation has also been noted in the Cu-systems (entry 10 vs entries 6-9). The reason for such observations can be attributed to that in the aryl substituted systems, the conjugation between the aryl π orbital and the π orbital of the SO₂ group (Figure 3), and the d orbitals of the metal center provide extra-stabilities to the concerned transition states. In contrast, such conjugation is unavailable in the alkyl systems, and therefore the relative activation barrier of alkyl systems is slightly higher than the related aryl ones. This proposal is also supported by relatively longer C-[M] bond distances in the alkyl substituted transition state (relative to the related ones in the aryl substituted transition state, Figure 4).

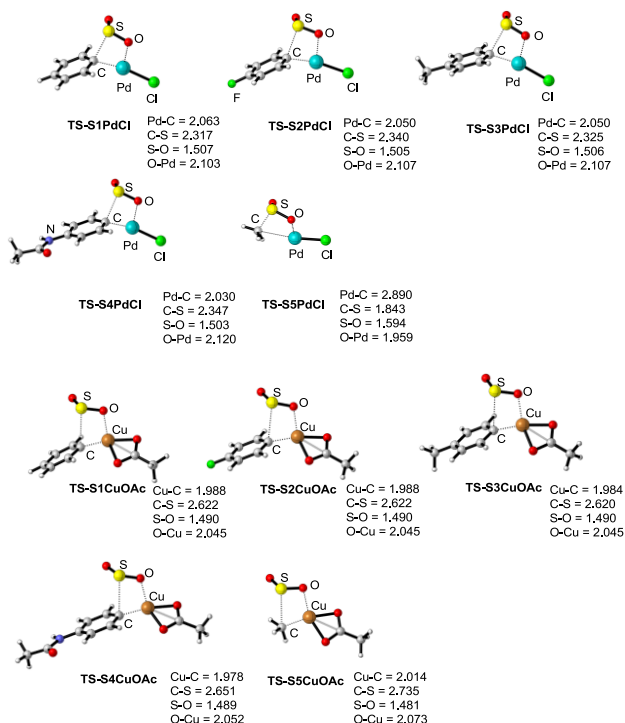


Figure 4. Optimized structures of TS-Sn[M] (n=1-5, [M]=PdCl, Cu(OAc)). The bond distance is given in angstrom.

3. Conclusions

Recently sulfinic acid and sulfinic acid salts have shown great potential in organic and bioorganic synthesis. C-SO₂R bond dissociation has been found to be involved in many of these reactions, and in some cases the ease of the bond dissociation is determinant to the overall reaction rates and selectivity. The primary goal of our study is to clarify a reliable DFT method in accurately predict the C-SO₂R BDEs. The following conclusions have been generated:

- (1) M05-2X, M06-2X and M06 methods were found to be relatively more accurate than all the other studied methods (B3LYP, BB1K, M05, M06-L, MPW3LYP, MPWB1K, PBE, TPSS, and TPSSLYP1W) in reproducing the C-S BDEs. In contrast, 7 studied DFT methods (including BB1K, MPW1K, MPW3LYP, MPWB1K, PBE, TPSS, TPSSLYP1W) were found to give relatively large deviations (from the experimental results), and are suggested to be used with caution in treating the reaction systems involving the C-S bond dissociations. What's more, M05-2X and M06-2X are found to be slightly more accurate than M06 in calculating the C-SO₂R BDEs.
- (2) With M05-2X or M06-2X methods, the performance of different basis sets (6-31G(d), 6-31G(d,p), 6-31+G(d,p), 6-311+G(d,p), 6-311++G(d,p), 6-311++G(2df,2p)) are all comparable. The results indicate that the 6-31G(d) might be a good choice from both accuracy and computational cost aspects.
- (3) Primary mechanistic studies have been performed on the desulfinitative step in the chemoselective coupling or desulfinitative coupling reactions in presence of either Cu or Pd (Pd-Cu) systems. It's found that both reaction systems undergo the concerted desulfinitative step, and the strong CSO₂-[Cu] bond strength is mainly responsible for the difficult desulfinitative step in the Cu-catalyzed system.

Calculation methods

All calculations in this study were carried out on Gaussian 09 platform.³³ Geometry optimization and frequency calculations are all performed in gas phase, corresponding to the experimental conditions. The examination on the 13 different DFT functionals are carried out with the 6-31G(d) basis set, and the basis set effect examinations were carried out with the clarified M05-2X and M06-2X methods. Finally, M06-2X/6-31G(d) method is used for the mechanistic studies on the desulfinitative steps in Cu- and Pd-catalyzed systems, and the gas-phase calculations are used to simulate the situations in the solution phase in previous experiments.^{4,6} All species in the present study are calculated at 298.15 K under 1 atm atmosphere. The total electronic energy corrected by the thermal correction to enthalpy are used to describe all the enthalpies.

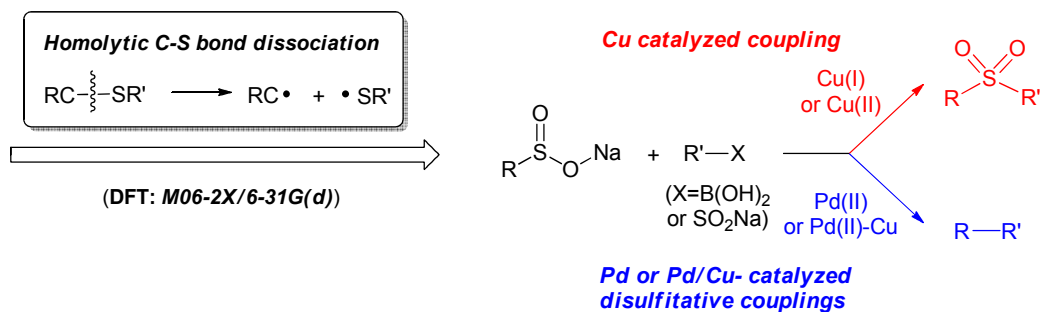
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Notes and references

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M06-2X/6-31G(d) was found to be accurate in calculating C-S BDEs, and preliminary mechanistic studies were performed with it.