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Abstract

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Disciplines

Chemistry | Organic Chemistry | Other Chemistry | Polymer Chemistry

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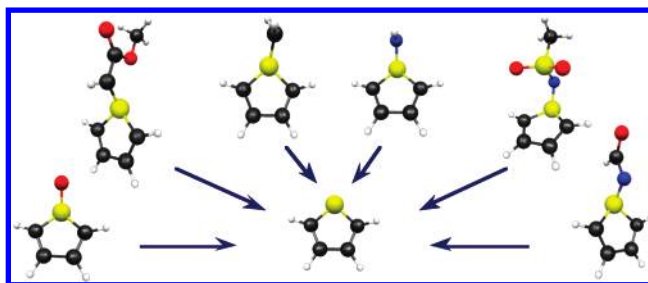
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Sulfur and Selenium Ylide Bond Enthalpies

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The bond dissociation enthalpies (BDEs) of sulfur and selenium ylides have been estimated by applying MP2/6-311++G(3df,2p)//MP2/6-31G(d,p), G3, and other computational methods. Computed sulfoxide bond enthalpies were compared to experimental results to ensure the reliability of the computational methods before extending to related compounds. The examined ylides include the following: sulfoxides, sulfilimines, *S,C*-sulfonium ylides, and selenoxides. Selenoxides have BDEs about 10 kcal/mol smaller than the corresponding sulfoxides. *N*-H sulfilimines and CH$_2$-*S,C*-sulfonium ylides have low BDEs, unless the sulfilimine or *S,C*-sulfonium ylide is stabilized by an electronegative substituent on N or C, respectively. Incorporation of the S or Se into a thiophene or selenophene-type ring lowers the BDE for the ylide.

Introduction

Sulfur and selenium ylides of various sorts are useful compounds in organic chemistry.[1-9] Our own interests have focused on the chemistry and photochemistry of a common ylide, the sulfoxide. In particular, we have been interested in the formation of atomic oxygen, O(^{3}P), by means of photolysis of dibenzothiphene-*S*-oxide and dibenzoselenophene-*Se*-oxide.[10-14]

In separate publications, we will additionally present evidence for the formation of nitrenes and carbenes upon photolysis of related sufilimines and *S,C*-sulfonium ylides.

Ch = S, Se
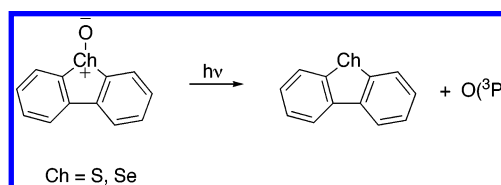
From a mechanistic perspective for such reactions,[15-22] the bond dissociation enthalpy (BDE) of the sulfur ylide bond is critical to help determine whether unimolecular dissociation is plausible. One needs to know whether the lowest triplet and singlet excited states are sufficiently energetic to activate the cleavage. Unlike other sulfur and selenium ylides, detailed

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thermochemical data allowing calculation of sulfoxide bond strengths are available for representative compounds.[23–30] Standard sulfoxide S—O BDEs are on the order of 87–90 kcal/mol. Electronegative substituents raise the bond strength; for example, the BDE for F_2SO is 114 kcal/mol.[28] Intramolecular interactions between heteroatoms in a saturated ring can affect S—O BDEs.[31,32] On the other hand, conjugation of the sulfoxide to phenyl or vinyl substituents does not have a large effect.[29] However, the S—O bond strengths of thiophene derivatives are weakened because of the extra stabilization of the thiophene ring, compared to the nonaromatic sulfoxides. Previous calculations predict a BDE of about 65 kcal/mol for thiophene-*S*-oxide.[29]

Comparable experimental data are not available for sulfilimines (nitrogen ylides) or *S,C*-sulfonium ylides (carbon ylides), although discussion of the type of bonding in sulfilimines, parallel to the descriptions of sulfoxides, has appeared.[24,33,34] An older study estimated the BDE of the S—CH_2 bond in H_2SCH_2 to be 27.5 kcal/mol with use of MP3/6-31G(d,p),[35] but a more recent G2 calculation for dimethylsulfonium methylide put the BDE at 51 kcal/mol for dissociation to singlet methylene,[36] which is about 9 kcal/mol above the triplet methylene ground state. To the best of our knowledge, there are no reports on the BDEs of sulfilimines or selenoxides. In this paper, we report estimates of the BDEs for a variety of model sulfilimines, *S,C*-sulfonium ylides, sulfoxides, and their selenium analogues. Because of the size of the molecules, we use a set of empirically determined methods based on ab initio calculations to arrive at reasonable estimates of the ylide-like BDE for a number of compounds. We explore the effect of electron-withdrawing substituents, which are typical in the most commonly observed compounds.

Computational Methods

Initial geometries were acquired from the lowest energy conformation obtained from a semiempirical (PM3) conforma-tional search performed with MacSpartan.[37] Geometries were then optimized at the MP2/6-31G(d,p) level. All further calculations were carried out at this geometry. All sulfur ylide geometry optimizations were performed with the GAMESS suite of programs[38] and the results were visualized with MacMolPlt.[39] Geometries of Se-containing compounds were obtained with Gaussian03[40] and visualized with GaussviewM. All geometries were confirmed as minima by calculating the vibrational frequencies, and the reported ΔH values include unscaled zero point energies (ZPEs) and a temperature correction at 298.15 K. The G3 calculations[41–43] for Se-containing compounds were done manually (with Gaussian03), whereas the rest were done with the automated G3 input. Coefficients and exponents for the G3Large basis set for selenium were obtained from http://chemistry.anl.gov/compmat/g3theory.htm.

Results and Discussion

A decided benefit of computational chemistry is the ability to calculate thermochemical data for experimentally inaccessible or untested molecules. That said, a distinct disadvantage is that we are not yet at the point that the ordinary chemist is able to do arbitrarily good calculations on groups of even moderate-sized molecules from the perspective of the organic chemist. This is a particular problem for certain quantities, such as the one addressed here, BDEs. The challenge derives, at least in part, from the fact that most BDEs involve non-isogyric reactions (e.g., producing radicals from closed shell molecules) that highlight some of the shortcomings of the less expensive computational methods.

For dissociations of Ch—E ylide-type bonds, of which the sulfoxide S—O bond is the archetypal example, there are at least two difficulties. First, the ground state products generally include a triplet species (e.g., O(^{3}P)), meaning the reactions are not isogyric. Second, it is well-established that oxides of sulfur require extensive basis sets to obtain accurate energies.[44–51]

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The stability of sulfur oxides is typically underestimated without these large basis sets. At a minimum, "tight valence" d-polarization functions (e.g., "3d" in the Pople basis set notation) are required for qualitative results, and the most accurate results require even tighter core polarization functions. There is every reason to believe that these difficulties would extend to other sulfur/selenium ylides, e.g., sulfilimines and *S,C*-sulfonium ylides.

One reasonable way around these difficulties is the use of isodesmic reactions which allow for the maximal cancellation of errors. This can be done for a series of very closely related molecules, and absolute values can be obtained from experimental data for benchmark reactions. Our earlier work, in which we examined the sulfoxide bond strength as a function of substitution, used this approach with the well-established experimental data for dimethyl sulfoxide as the reference.[29,52,53]
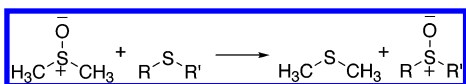
However, for the broader group of compounds that we now report, it was clear that the standard isodesmic approach would not work in most cases, because there are so few known experimental data. We are unaware of even a single case in which the heats of formation of a corresponding sulfilimine, sulfide, and nitrene are all known.

Thus the approach we take here is empirical, based on obtaining a balance between accuracy and practical achievability, recognizing that we must calculate the energies of non-isodesmic, non-isogyric reactions for some fairly large molecules. It is clearly beyond our ability to do the kinds of calculations that have been carried out most rigorously for molecules of the size of SO_2 and SO_3 on larger systems. Our approach is to use as many isodesmic reactions as possible. For reference reactions with sulfoxides, we use experimental data. For the other compounds, we establish a reference value using calculations done for a small "parent" compound. We believe that, even if allowances of a few kilocalories per mole must be made, the data outlined below are useful first estimates of BDEs for these compounds.

Establishing a Base Method for Sulfoxides. Experimental data are available for compounds **1**−**4** and the corresponding sulfides, so bond enthalpies at 298.15 K can be calculated.[53] We approached these compounds in order to develop primary "standard methods" that could be used with other molecules. Calculations were done by using MP2 and B3LYP with various basis sets including tight valence polariza-

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TABLE 1. Difference between Computational and Experimental S−O BDEs for Sulfoxides 1−4 (in kcal/mol)[a]

method[b]	1	2	3	4
experimental[c]	86.5 ± 0.5	88.8 ± 0.6	88.7 ± 1.2	89.3 ± 1.4
MP2/6-311++G(3df,2p)	3.1	−0.1	−1.3	−4.2
MP2/6-311G(3df,2p)	1.6	−1.0	−2.2	−4.0
MP2/6-311++G(d)	−18.6	−21.4	−22.5	−26.2
MP2/6-31+G(2d,p)	−8.1	−10.8	−11.8	−14.6
MP2/6-31G(2d)	−13.1	−14.9	−16.0	−17.2
MP2/6-31G(d,p)	−19.2	−21.2	−22.0	−23.3
MP2/6-311G(d)	−22.2	−23.8	−24.8	−26.6
MP2/6-31+G(d)	−13.9	−16.8	−17.7	−21.1
MP2/6-31G(d)	−18.8	−20.8	−21.7	−23.2
B3LYP/6-311++G(3df,2p)	−4.6	−8.0	−8.8	−11.6
B3LYP/6-311G(3df,2p)	−4.6	−7.5	−8.2	−10.1
B3LYP/6-311++G(d)	−19.3	−22.0	−22.7	−25.2
B3LYP/6-31+G(2d,p)	−11.4	−14.7	−15.4	−18.1
B3LYP/6-31G(2d)	−14.4	−16.8	−17.4	−18.6
B3LYP/6-31G(d,p)	−18.6	−20.7	−21.4	−22.5
B3LYP/6-311G(d)	−20.9	−23.4	−23.1	−24.3
B3LYP/6-31+G(d)	−17.2	−20.2	−20.8	−23.5
B3LYP/6-31G(d)	−18.6	−20.8	−21.4	−22.7
G3	−4.2	−7.0	−7.9	N/A

[a] A positive number corresponds to an overestimation and a negative number an underestimation of the BDE. [b] All ΔH values were determined from the listed method single point energy runs performed at the MP2/6-31G(d,p) optimized geometry and include the unscaled ZPE and the 298.15 K temperature correction. [c] Experimental BDEs were determined from the ΔH of S−O dissociation, using $\Delta H_f°$ values from the NIST webbook.

tion. Additionally, the G3 method, whose "G3Large" basis set includes core polarization, was used. Pople-style basis sets, rather than Dunning-style cc basis sets, were used, because the predominant factor in qualitative accuracy is the presence of adequate polarization functions, rather than large underlying valence functions. Results are shown in Table 1, with the first entry being the experimental value, and the remaining entries reflecting the error of the given method, where positive numbers imply an overestimation of the BDE. The data confirm that the difference in error between double- and triple-ζ basis sets is small, compared to the changes observed with polarization function increase.
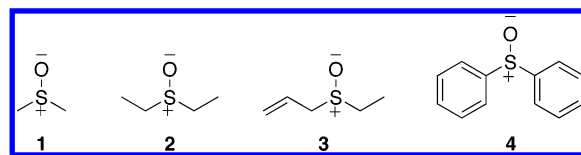
For all four molecules, MP2 calculations with three d-polarization functions are within about 4 kcal/mol, overestimating the bond strength for DMSO and underestimating that of Ph_2SO. B3LYP calculations show the same general trend, but consistently underestimate the dissociation enthalpy. G3 results are only available for sulfoxides **1**−**3**. While expected to have the greatest accuracy, G3 underestimates the S−O bond strength by a range of 4.2 to 7.9 kcal/mol. A disturbing result is that all of the methods predict that dimethyl sulfoxide has the strongest bond and diphenyl sulfoxide has the weakest, which is the opposite of the reported experimental values.

However, we can minimize the scatter in the data empirically by averaging some of the best calculations. The average error of the calculations is reduced to 2.1 kcal/mol if one averages the BDEs obtained from G3, MP2/6-311++G(3df,2p) and MP2/6-311(3df,2p). Not coincidentally, these two MP2 calculations are also the methods that give the values closest to experiment

TABLE 2. Computed S−O BDEs for Sulfoxides 5−9 (in kcal/mol)

method[a]	5	6	7	8	9
MP2/6-311++G(3df,2p)	89.3	86.0	60.4	67.3	72.1
MP2/6-311G(3df,2p)	86.5	85.5	59.6	66.4	71.3
B3LYP/6-311++G(3df,2p)	80.7	77.8	56.4		
B3LYP/6-311G(3df,2p)	80.9	78.7	57.0		
G3	79.1	79.0	56.6		
Method A[b]	87.1	85.6	60.9		
Method B:[c] MP2/6-311++G(3df,2p)	89.9	86.7	61.1	67.9	72.7
Method B: MP2/6-311G(3df,2p)	87.9	86.9	61.0	67.8	72.7
Method B: MP2/6-31G(d,p)	87.2	87.3	63.7	70.4	75.2
Method B: B3LYP/6-311++G(3df,2p)	88.9	86.1	64.7		
Method B: G3	85.4	85.3	62.9		

[a] All ΔH values were determined from the listed method single point energy runs performed at the MP2/6-31G(d,p) optimized geometry and include the unscaled ZPE and the 298.15 K temperature correction. [b] Average of MP2/6-311++G(3df,2p), MP2/6-311G(3df,2p), and G3, plus 2.1 kcal/mol. [c] Method B is the average of the BDE determined from four isodesmic reactions, using **1** (BDE$_{std}$ = 86.5 kcal/mol), **2** (BDE$_{std}$ = 88.8 kcal/mol), **3** (BDE$_{std}$ = 88.7 kcal/mol), and **4** (BDE$_{std}$ = 89.3 kcal/mol) as the standard sulfoxide.

for **2** and **3**, and **1** and **4**, respectively. Also, in a sense, this can be viewed as an arbitrary tweak to the Gn methods, whose philosophy is to sum several calculations to approximate the value that would be obtained at a particular higher level calculation with a large basis set. Thus we define an empirical "Method A" for estimation of the BDE as the average of the values from MP2/6-311++G(3df,2p), MP2/6-311(3df,2p), and G3, plus 2.1 kcal/mol. We take this to be the best estimate available for all molecules in our data set to which it can be applied.

Expanding to Other Sulfoxides. Sulfoxides **5−9** are compounds that were investigated previously, using the isodesmic approach with DMSO as a standard,[29] though experimental results are not available. Method A can be applied to molecules **5−7**, but not **8** and **9**, which are too large for practical G3 computations at this time. However, we can use compounds **1−4** as references for isodesmic reactions involving **5−7**.
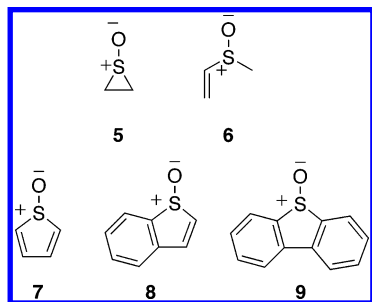

Because the computations for **1−4** showed inconsistent errors, we believed that the best approach to obtain BDEs for **5−7** would be to average the four possible isodesmic reactions for a given test molecule, using each of **1−4** as the reference. We define this as "Method B", where we must also stipulate the level of theory at which the isodesmic reaction was calculated. Here, the choice of computational method is less important because the errors tend to cancel out. Data in the Supporting Information show this to be the case for a larger set of calculations, and data obtained with the better basis sets are provided in Table 2.

Sulfilimines. Following the analogy to sulfoxides, sulfilimines can formally dissociate to sulfides and nitrenes. Although most experimentally relevant sulfilimines are *N*-substituted with

TABLE 3. Calculated S−N BDEs to Form ³NH and the Corresponding Sulfide (in kcal/mol)

method[a]	10	11	12	13	14	15
MP2/6-311++G(3df,2p)	47.5	25.5	43.1	34.2	38.3	42.4
MP2/6-311G(3df,2p)	46.2	23.3	41.2	33.2	37.0	41.5
B3LYP/6-311++G(3df,2p)	39.6	20.3	37.1	27.3	32.0	34.5
B3LYP /6-311G(3df,2p)	39.4	19.2	36.4	27.3	31.7	34.7
G3	39.2	17.8	35.0	23.8	30.3	34.5
Method A	46.4	24.3	41.9	32.5	37.3	41.6

[a] All ΔH values were determined from the listed method single point energy runs performed at the MP2/6-31G(d,p) optimized geometry and include the unscaled ZPE and the 298.15 K temperature correction.
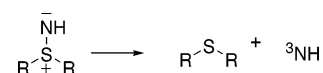
electron-withdrawing groups, we chose to begin this exploration of the thermochemistry with the parent *N*-H sulfilimines **10−18**. On the basis of the notion that nitrogen is less electronegative than O, our initial assumption was that the bond enthalpy would be lower for sulfilimines than for sulfoxides, but we did not know by how much. Because the ground states of simple nitrenes are triplets, the dissociation reactions are again neither isogyric nor isodesmic. Worse, there are not sufficient experimental data to establish appropriate reference benchmarks. Thus, we rely on some of the patterns established for the sulfoxides.
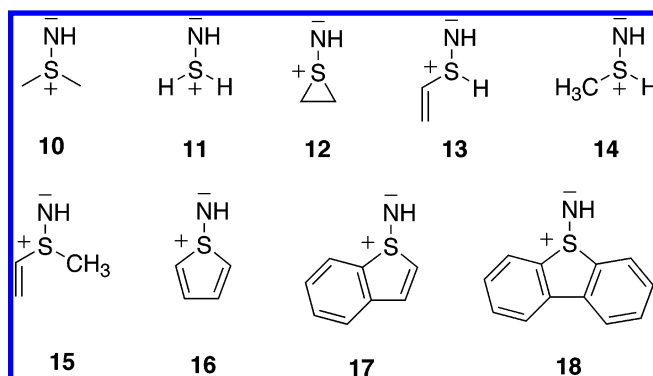
Of the sulfilimines **10−18**, G3 calculations were carried out for **10−15**. The enthalpies of the dissociation reactions, calculated at several levels including G3 and with Method A (defined above in the sulfoxide case), are shown in Table 3. The results are approximately 40 kcal/mol lower than those for the corresponding sulfoxide.

How to treat compounds **16−18** is another question that must be addressed empirically, because they are too large for G3 calculations, and therefore cannot be treated by Method A. Using the results for compounds **10−15** as benchmarks, we looked for a single calculation that best tracked Method A and thus would be used in isodesmic reactions for **16−18**. The MP2/6-311++G(3df,2p) calculations give higher BDEs than Method A by an average of 0.6 kcal/mol, but the standard deviation of that difference is only 0.8 kcal/mol. Thus, very similar BDEs for **11−15** would be obtained by either (a) using compound **10** and its Method A BDE for a reference in an isodesmic reaction between **11−15** and dimethyl sulfide (the base sulfide of **10**) or (b) calculating the BDE for **11−15** directly by Method A. We thus define this as Method C for determining a BDE: an isodesmic reaction, calculated at

the MP2/6-311++G(3df,2p) level, between the large test compound (e.g., **16**) and a parent molecule (e.g., **10**), where the parent compound's BDE, calculated with Method A, is used as the reference value. In subsequent paragraphs, we will present other data using Method C, based on different parent compounds, e.g., dimethyl selenoxide for various Se−O BDEs. Complete data are shown in the Supporting Information. With Method C, the BDEs are 21.4, 28.7, and 33.4 kcal/mol for **16**, **17**, and **18**, respectively.

S,C-Sulfonium Ylides. A similar approach was taken for sulfonium methylides **19**−**26** in the formation of methylene. Again, there are no good experimental data to use for comparison to calculations.
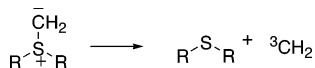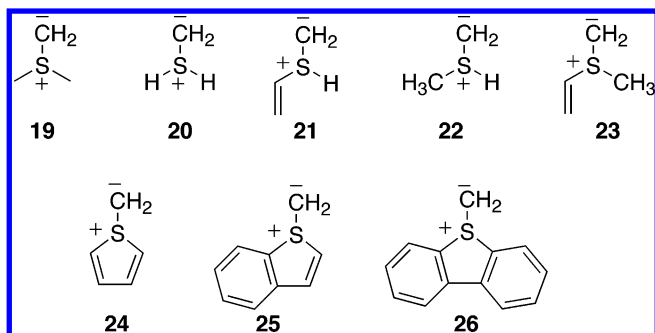

Table 4 shows data obtained for **19**−**23** and the BDEs obtained with Method A. We again use Method C for the larger compounds, i.e., using an isodesmic reaction of **24**−**26** with compound **19** as the reference dissociation reaction. The resulting BDEs for **24**−**26** with Method C are 24.2, 31.4, and 36.8 kcal/mol, respectively.


Selenoxides. In Table 5 are the data, similarly obtained, for the dissociation of selenoxides **27**−**29** to form the corresponding selenides and O(^{3}P). The use of dimethyl selenoxide (**27**) as the standard for an isodesmic reaction with MP2/6-311++G-(3df,2p) energies allows us to estimate bond enthalpies of **30**, **31**, and **32** using Method C as 57.5, 59.8, and 64.2 kcal/mol, respectively.
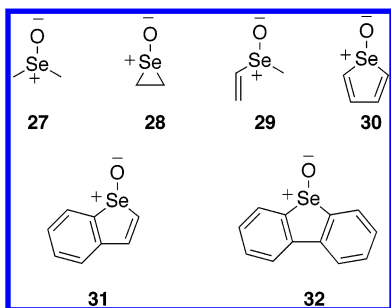

Substituted Sulfilimines and S,C-Sulfonium Ylides. The sulfilimines and S,C-sulfonium ylides that are most straightforward to prepare and handle in the laboratory are not those that have been shown in the previous cases with no N- or C-substitution, but those bearing electron-withdrawing groups.[54] In principle, this could be due to hydrolytic (kinetic)

stability, but it also stands to reason that electron-withdrawing groups would increase the bond dissociation enthalpy toward nitrene/carbene formation by stabilizing the formal negative charge on the N or C. Thus, we calculated BDEs for compounds **33**−**42**.
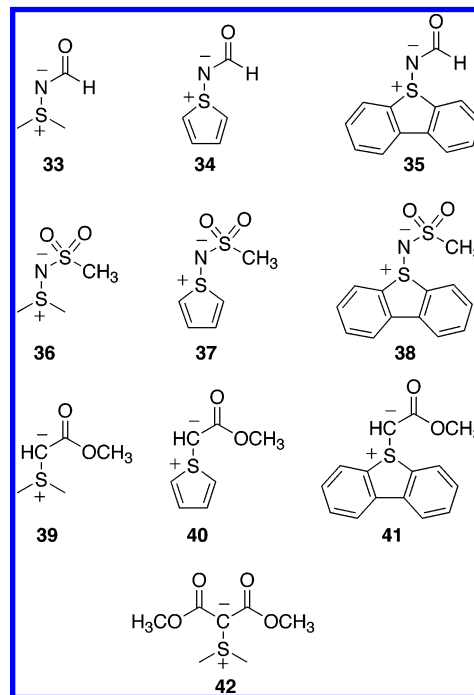
Estimates of the BDEs for these compounds were obtained from isodesmic reactions as well, using compound **40** as an illustration. The base calculations were done at the MP2/6-311++G(3df,2p) level, and the reference BDE used was the best available (Method A or C) for the corresponding *N*H-sulfilimine or *C*H₂-sulfonium ylide. For **40**, the reference was the BDE reported for **24** with Method A. The values are reported in Tables 6 and 7.
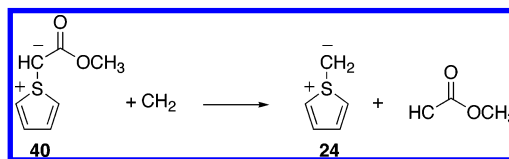
An additional complication for the nitrenes is that the groups that stabilize the ylide also exert substantial stabilization to the hypovalent intermediates, especially the singlet states. In fact, while the ground state of the parent nitrene NH is the open shell triplet, by 36 kcal/mol, the ground state of several α-carbonyl nitrenes, as established by rigorous computational work, is the closed-shell singlet, due to what might be called a partial bond between the oxygen atom and the nitrogen, using the oxygen lone pair and the formally empty orbital on the nitrogen.[53−57] (No currently available experimental or computational evidence suggests that the sulfonyl nitrenes have singlet ground states.) Such stabilization is considerably less important

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(57) Block, E.; Clive, D. L. J.; Furukawa, N.; Oae, S. *Org. Compd. Sulphur, Selenium, Tellurium* **1981**, *6*, 79−147.

TABLE 4. Calculated S−C BDEs to Form ³CH₂ and the Corresponding Sulfide (in kcal/mol)

method[a]	19	20	21	22	23
MP2/6-311++G(3df,2p)	45.8	26.5	33.7	38.4	43.6
MP2/6-311G(3df,2p)	44.9	25.6	32.9	37.5	43.1
B3LYP/6-311++G(3df,2p)	40.4	24.7	29.4	34.7	37.2
B3LYP/6-311G(3df,2p)	40.1	24.5	29.4	34.5	37.4
G3	40.6	22.3	29.2	33.6	38.1
Method A	45.9	26.9	34.0	38.6	43.7

[a] All ΔH values were determined from the listed method single point energy runs performed at the MP2/6-31G(d,p) optimized geometry and include the unscaled ZPE and the 298.15 K temperature correction.

for the triplet states of carbonyl nitrenes, in which the *N*-centered orbital is half-filled and the extra bonding interaction is attenuated. For the substituted carbenes implied in compounds **39**−**42** (Table 7), we are unaware of any evidence that the ground state is other than a triplet.

Thus, in Table 6, a second, slightly lower BDE is given in parentheses for compounds **33**−**35**. This is the BDE to give the singlet formylnitrene, where the singlet is taken to be 0.7 kcal/mol lower in energy on the basis of reported calculations at the CCSD(T)/cc-pVTZ level extrapolated to an infinite basis set.[57]

Chemical Interpretations. We now turn to a discussion of several trends revealed in the data. Among these are (a) trends within a structure type, based on the underlying sulfide/selenide, (b) trends between sulfoxide, sulfilimine, *S,C*-sulfonium ylide, and selenoxide for the same underlying sulfide/selenide, and (c) trends for *N*- or *C*-substitution on sulfilimines and *S,C*-sulfonium ylides. It is beyond the scope of this paper to quantitatively parse various contributions to the estimated BDEs; nonetheless the trends are important, and we can make attractive speculative arguments.

Table 8 illustrates the relevant data. The computations consistently give a slightly lower BDE for the conjugated methyl vinyl derivative than for the dimethyl derivative for each structure type. Were it not for the experimental value available for diphenyl sulfoxide that *exceeds* the BDE of dimethyl sulfide by 2.8 kcal/mol, it would be tempting to conclude that there was a genuine, if not large, effect on the ylide BDEs by conjugation. With the present data, however, this will have to await either better calculations or additional experimental work.

It is unambiguous, however, that there is a major effect on the BDEs that is based on the aromaticity of the underlying sulfide (entries 3−5). Cleavage of the sulfoxide, sulfilimine, *S,C*-sulfonium ylide, or selenoxide always results in a "more" aromatic product, as illustrated for compounds **16** and **17**.
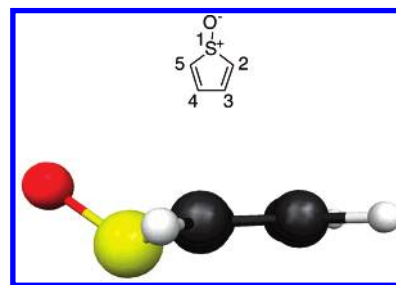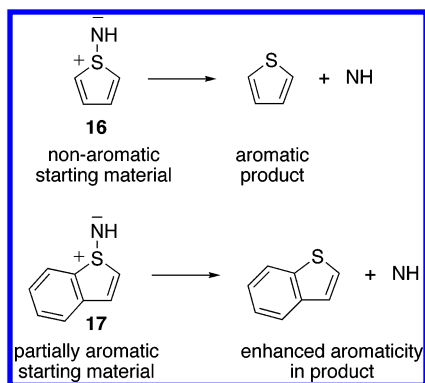
FIGURE 1. Out-of-plane sulfur geometry at MP2/6-31G(d,p).

TABLE 5. Calculated Se−O BDEs for 27−29 (in kcal/mol)

method[a]	27	28	29
MP2/6-311++G(3df,2p)	79.1	75.7	74.6
MP2/6-311G(3df,2p)	78.5	75.2	74.4
B3LYP/6-311++G(3df,2p)	69.6	68.5	65.5
B3LYP /6-311G(3df,2p)	70.3	69.3	61.0
G3	70.2	68.9	66.3
Method A	78.0	75.4	73.9

[a] All ΔH values were determined from the listed method single point energy runs performed at the MP2/6-31G(d,p) optimized geometry and include the unscaled ZPE and the 298.15 K temperature correction.

TABLE 6. Estimated S−N BDEs for Substituted Sulfilimines

method[a]	33	34	35	36	37	38
MP2/6-311++G(3df,2p)// MP2/6-31G(d,p)	81.2 (80.5)	52.9 (52.2)	71.7 (71.0)	70.2	47.7	62.1

[a] All ΔH were determined from isodesmic reactions with *N*H, and include the unscaled ZPE and the 298.15 K temperature correction. The reference reaction is the corresponding dissociation of the analogous *N*H-sulfilimine, whose energy was taken from Method A or C, as appropriate.

TABLE 7. Estimated S−C BDEs for Substituted *S,C*-Sulfonium Ylides

method[a]	39	40	41	42
MP2/6-311++G(3df,2p)// MP2/6-31G(d,p)	61.5	39.0	54.5	68.8

[a] All ΔH were determined from isodesmic reactions with CH₂, and include the unscaled ZPE and the 298.15 K temperature correction. The reference reaction is the corresponding dissociation of the analogous CH₂-sulfonium ylide, whose energy was taken from Method A or C, as appropriate.

Even if we postulate that thiophene-*S*-oxide is essentially nonaromatic (similar to cyclopentadiene), it may be an oversimplification to say the same for the corresponding sulfilimine (**16**) or *S,C*-sulfonium ylide (**24**). The bond destabilizations for the latter two compounds (23.4 and 20.1 kcal/mol), compared to the respective dimethyl sulfide compounds, are somewhat smaller than the bond destabilization of 25.6 kcal/mol for the sulfoxide. Although **16** and **24** and their analogues certainly have a largely reduced aromatic stabilization compared to thiophene, there is some structural evidence that they may retain more than does thiophene-*S*-oxide itself. It is well-known that the sulfur atom in thiophene-*S*-oxide derivatives "dips" below the plane of the carbon atoms in the rest of the ring.[29,55] This is simply a variation of the standard "envelope" conformation of 5-membered rings. Such a dip minimizes interactions of the sulfur atom orbitals with the rest of the π system and obviously goes to zero in the limit of thiophene (or selenophene). A similar phenomenon has been experimentally demonstrated by Nakayama for *N*-tosyl-3,4-di-*tert*-butylthiophene sulfilimine, a compound closely related to **37**.[56]

TABLE 8. Comparison of BDEs Based on the Underlying Sulfide/Selenide

		BDE (difference from dimethyl parent), kcal/mol			
entry	sulfide (or selenide)	sulfoxide	*N*-H sulfilimine	*C*-H$_2$ sulfonium	selenoxide
1	dimethyl sulfide (selenide)	86.5^a	44.8^b	44.3^b	76.4^b
2	methyl vinyl sulfide (selenide)	85.6^b (−0.9)	41.6^b (−3.2)	43.7^b (−0.6)	73.9^b (−2.5)
3	thiophene (selenophene)	60.9^b (−25.6)	21.4^d (−23.4)	24.2^d (−20.1)	57.5^d (−18.9)
4	benzothiophene (benzoselenophene)	67.9^c (−18.6)	28.7^d (−16.1)	31.4^d (−12.9)	59.8^d (−16.6)
5	dibenzothiophene (dibenzoselenophene)	72.7^c (−13.8)	33.4^d (−11.4)	36.8^d (−7.5)	64.2^d (−12.2)

^{a} Experimental value. ^{b} Method A. ^{c} Method B: MP2/6-311++G(3df,2p). ^{d} Method C.

TABLE 9. Heats of Insertion of Methylene, Imidogen, and Oxene

no.	reaction	$\Delta H°$ (kcal/mol)^a
1	CH$_2$ + H$_2$ → CH$_4$	−110.3
2	NH + H$_2$ → NH$_3$	−101.0
3	O + H$_2$ → OH$_2$	−117.4
4	CH$_2$ + CH$_3$-CH$_3$ → CH$_3$-CH$_2$-CH$_3$	−97.4
5	NH + CH$_3$-CH$_3$ → CH$_3$-NH-CH$_3$	−74.4
6	O + CH$_3$-CH$_3$ → CH$_3$-O-CH$_3$	−83.6

^{a} Data taken from heats of formation from the NIST webbook.

The dihedral angle 1(S),2,3,4 as illustrated in Figure 1 is indicative of how far below the plane the sulfur atom resides, as calculated at the MP2/6-31G(d,p) level. These angles are 9.9°, 7.3°, and 5.3° for the oxide, sulfilimine, and methylide of thiophene, respectively, at their MP2/6-31G(d,p) optimized geometries. This trend is consistent with the descending destabilization of the thiophene-based sulfoxide, sulfilimine, and *S,C*-sulfonium ylides, when compared to the corresponding dimethyl sulfide-based sulfide, sulfilimine, and *S,C*-sulfonium ylide. The angle for mesyl derivative **37** is calculated to be 8.2°. Its BDE is intermediate between those of thiophene sulfilimine and thiophene-*S*-oxide, just as this dihedral angle is.

The bond destabilization effect of thiophene is attenuated with benzannulation in a qualitatively consistent manner across all of the compounds. We assert that the origins of this effect come from the quantitatively smaller energy of aromaticity of the "second" ring of benzothiophene and "third" central ring of dibenzothiophene. It is of course widely recognized that anthracene is more reactive than naphthalene, which is in turn more reactive than benzene, for this same reason. Note that we speak not of a "per carbon" level of aromatic stabilization, but rather the total aromatic stabilization energy that is lost on dearomatization of one ring of the fused compounds.

Next, we consider the series of compounds in the other dimension, i.e., comparing sulfoxide to sulfilimine to sulfonium and selenoxide. As alluded to earlier, because of the ylide nature of the bonds, it is not surprising that the sulfoxide is the strongest bond among the sulfoxide, sulfilimine, and sulfonium ylide. Upon dissociation, the compound goes from a highly polar bond to a situation of no charge separation between the S and O (or NH or CH$_2$). Thus, the greater ability of O to stabilize negative charge (as reflected in its electronegativity) ought to lead to a stronger bond through greater relaxation of the S−O charge distribution. This is qualitatively reflected in the stronger sulfoxide bond, but the fact that the sulfonium ylide S−C bonds are consistently a few kilocalories per mole stronger than the sulfilimine S−N bonds is confounding.

However, at least a qualitative solution is reached when one considers the product side of the dissociation reaction. Underlying the above argument is the assumption that the "stability" of the hypovalent product (O, NH, or CH$_2$) is the same. One way to check this is to consider the heats of formation of other simple reactions with these compounds. In Table 9 are given the enthalpies of hydrogenation of O, NH, and CH$_2$, along with the enthalpies of insertion into the C−C bond of ethane.

Strikingly, although it is most exothermic to hydrogenate O (entry 3 among 1−3), and most exothermic to insert CH$_2$ into ethane (entry 4 among 4−6), it is least exothermic to hydrogenate or insert NH by 10−15 kcal/mol, compared to the other reactions. We can infer, then, that the nitrene is the most "stable" of the three hypovalent intermediates by 10−15 kcal/mol. This −10 to −15 kcal/mol contribution to the BDE of the sulfilimines in Table 8 can thus at least potentially explain why the sulfilimine S−NH and S−CH$_2$ BDEs are more comparable than originally expected.

Now, we turn to the substituted sulfilimines and *S,C*-sulfonium ylides. Many sulfilimines and *S,C*-sulfonium ylides are stable enough to be stored and handled, even the parent compounds in some instances. The parent *N*-H sulfilimines of many simple alkyl and aryl sulfides have been characterized for many years,[54] but in work to be published elsewhere, we will present the first characterization of **18**; we are unaware of the isolation and characterization of **16**. However, the clear majority of work involving sulfilimines and *S,C*-sulfonium ylides uses compounds with electron-withdrawing substituents on *N* or *C*, respectively.[54,57] The data clearly demonstrate that electron-withdrawing groups add to the stability of the sulfilimine or *S,C*-sulfonium ylide, presumably because delocalizing the charge in the starting material is a larger stabilizing effect than is any stabilization on the triplet nitrene or carbene.[58]

If the BDEs determined for *N*-formyl sulfilimines **33**−**35** are compared to the corresponding *N*-H derivatives **10**, **16**, and **18**, the S−N BDE is seen to increase by a remarkable 31−38 kcal/mol. These were chosen as representatives of the large group of *N*-acyl sulfilimines. Other acyl substituents, such as *N*-benzoyl and *N*-acetyl, would be expected to have BDEs within a few kilocalories per mole of the formyl derivatives.

The *N*-mesyl substituents of **36**−**38** were chosen to represent the family of *N*-mesyl, *N*-benzenesulfonyl, and *N*-tosyl sulfilimines in a similar fashion. The mesyl group has a slightly smaller effect on BDEs than does the formyl group, but it is still large. The S−N bonds are stronger for **36**−**38** by 24−29 kcal/mol than their *N*-H counterparts.

Because carbenes derived from precursors such as ethyl diazoacetate or dimethyl diazomalonate are comparatively common, we chose compounds **39**−**41** as models for the singly substituted case. Compared to their CH$_2$ analogues **19**, **24**, and **26**, respectively, the BDE enhancements are 15−18 kcal/mol. Adding a second carbomethoxy group, as with **42**, increases the BDE enhancement as expected, but to only about 23 kcal/mol (again, compared to the BDE of **19**).

(58) Carbonyl groups strongly stabilize the singlet state of the nitrene, but as noted previously, this only gets the nitrene singlet state to be near or just barely below the energy of the triplet nitrene.

Finally, we turn to the selenoxides. Like sulfoxides, sulfilimines, and *S,C*-sulfonium ylides, the BDEs of selenoxides are also only marginally affected by conjugation to a vinyl group. The selenophene derivatives have selenium−oxygen bond strengths that are lower than the corresponding sulfoxide bonds in the thiophene derivatives. Selenophene-*Se*-oxide has the weakest ylide bond, but it is only approximately 7 kcal/mol weaker than dibenzoselenophene-*Se*-oxide. The others are all about 10 kcal/mol weaker than the corresponding sulfoxide.

We have previously shown that photolysis of **32** produces an oxidizing agent we suggest is O(^{3}P).[12] The estimated BDE of 64.2 kcal/mol is thus particularly important, because it lies well below the singlet excited-state energy of **32**, but is also very close to the triplet energy we anticipate for **32**. Unfortunately, we have been unable to obtain phosphorescence data for dibenzoselenophene-*Se*-oxide, but the triplet energy of dibenzothiophene-*S*-oxide—which should be very similar—is about 60 kcal/mol.[59] It is thus at least possible that photochemical cleavage of O(^{3}P) may be induced from **32** from its triplet state. (Similar energetic arguments show that this is *not* the case for dibenzothiophene-*S*-oxide.) The observed quantum yield for photochemical deoxygenation of **32** is in the range of 0.1−0.3, depending on conditions, while that of dibenzothiophene-*S*-oxide ranges from 0.003 to 0.01. The possible compatibility of the lowest triplet energy of dibenzoselenophene-*Se*-oxide with the Se−O BDE may account for this much greater photochemical efficiency.

Summary

The determination of BDEs for sulfoxides, sulfilimines, and *S,C*-sulfonium ylides remains challenging. Recognizing the shortcomings of several individual computational approaches, we have taken an empirically devised method involving three sets of ab initio calculations as our "best estimate" for a variety of relatively small molecules in these classes. We have then taken the isodesmic approach to relate these BDEs to those of other, larger compounds. While we therefore do not claim a reliable "chemical accuracy" of 1−2 kcal/mol, we do believe the method does justify viewing these as reasonable first estimates for the unknown BDEs of compounds **5−42**.

In qualitative terms, the sulfoxides' S−O bond is the strongest of the ylide-type bonds, followed by Se−O in selenoxides, S−N in *N*-H sulfilimines, and S−C in *C*-H$_2$ *S,C*-sulfonium ylides. Inclusion of the sulfur atom in a thiophene ring lowers the BDE due to increased aromaticity in the thiophene products after S−O, S−N, or S−C cleavage. The data suggest that the *N*H-sulfilimine and the *C*H$_2$-sulfonium ylide of thiophene may, in fact, be very difficult to isolate at room temperature, due to BDEs of 21 and 24 kcal/mol.[60] The BDEs of the sulfilimines are increased by 31−38 kcal/mol by substitution of *N*-CHO for *N*-H or by 24−29 kcal/mol by use of a mesyl group. The substitution of a carbomethoxy group on the *S,C*-sulfonium ylide raises the BDE by 15−18 kcal/mol, with a smaller increment for a second carbomethoxy substitution.

Supporting Information Available: Geometries, absolute energies, and energy differences at several basis sets. This material is available free of charge via the Internet at http://pubs.acs.org.

(59) Jenks, W. S.; Lee, W.; Shutters, D. *J. Phys. Chem.* **1994**, *98*, 2282−2289.

(60) Thiophene sulfoxide itself cannot be isolated because of self-condensation reactions. However, alkyl substitution of the ring gives sufficient kinetic stabization against the self condensations that they may be handled and isolated. This type of self-condensation of the parent compounds would undoubtedly also plague the sulfilimine and *S,C*-sulfonium ylides.