Sulfene−Pyridine Adducts: Lewis Acid/Base Complexes, Ylides, Pyridinium Sulfinate Zwitterions, or Carbene Ylide/SO_2 Complexes?

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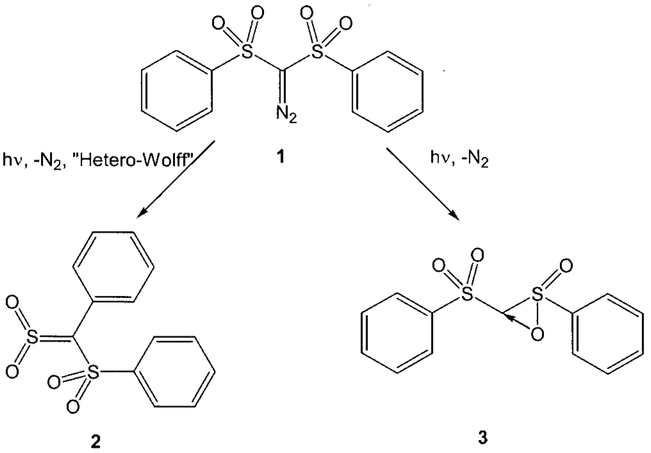
Dedicated to Prof. Günter Opitz on the occasion of his 77th birthday

Keywords: Density functional calculations / Lewis acids / Sulfenes / Ylides / Zwitterions

The reactions between a number of sulfenes and pyridine have been investigated by both density functional and ab initio theory. Two reaction channels were found. Addition of pyridine to the sulfene S atom produces products with the character of Lewis acid/base adducts. In polar solvents such as acetonitrile, scipcm calculations predict a shortening of the S–N bond with increasing ylide character, as revealed by long-wavelength absorptions predicted by time-dependent DFT calculations. Addition of pyridine to the sulfene C atom affords adducts better described as Lewis acid/base adducts between carbene pyridine ylides and SO_2 rather than as pyridinium sulfinate zwitterions. Again, scipcm calculations predict tighter binding in polar solvents. In the series of sulfene-pyridine adducts investigated, the C-bound adduct was consistently lower in energy than the S-bound adduct, by at least 15 kcal/mol. For the formation of the C-bound adducts an activation enthalpy of 14 kcal/mol or larger is calculated, while the formation of S-bound sulfene–pyridine adducts is predicted to proceed without any barrier. The S-bound adducts are therefore formed in kinetically controlled reactions, while the C-bound adducts are the thermodynamically favored products.

Introduction

Sulfenes, molecules of formula $RR'C{=}SO_2$, constitute an interesting class of highly reactive organosulfur compounds.[1,2] Reactions of sulfenes include cycloaddition reactions with olefins, yielding thietane-*S*,*S*-dioxides, and very fast reactions with nucleophiles, resulting in the formation of derivatives of sulfonic acids. The kinetics of sulfene/nucleophile reactions were recently investigated by Scaiano and co-workers,[3] who studied the photochemistry of bis(phenylsulfonyl)diazomethane **1** by laser flash photolysis (LFP). Upon excitation, diazo compound **1** undergoes dediazotization, accompanied in part by a hetero-Wolff rearrangement affording sulfene **2**. The latter reaction is likely to take place on the diazo excited state surface,[4a] thus bypassing the singlet carbene intermediate. Other reactions of excited **1** include formation of oxathiirene *S*-oxide **3** (Scheme 1[4b]), which decays further through complex follow-up reactions.[4a]



Scheme 1

If the incoming nucleophile does not bear an acidic hydrogen atom, as in the case of pyridine, for example, deprotonation to form a stable sulfonic acid derivative is not possible, bipolar structures being formed instead. Unlike the related pyridine−SO_3 complex,[5] which has been characterized structurally by microwave spectroscopy, little is known about such sulfene−pyridine adducts. Knunyants, Sokol'skii, and co-workers have reported on the formation

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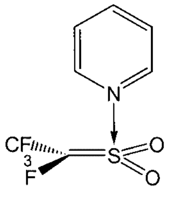
of the adduct **4** of fluoro(trifluoromethyl)sulfene ($F_3CCF=SO_2$) with pyridine, which was described as "white coarse needle crystals with m.p. 134 °C".[6] Its characterization was based solely on an elemental analysis, no further spectroscopic or structural information (NMR, IR, UV/Vis, MS, or X-ray) being given. Adducts of electron acceptor-substituted sulfenes with Lewis bases stronger than pyridine, such as the adducts of mesylsulfene with trimethylamine[7] or quinuclidine[8] and the bis(trifluoromethyl)sulfene−quinuclidine adduct,[9,10] have been characterized by NMR and X-ray crystallography. In the case of the quinuclidine−mesylsulfene and quinuclidine−bis(trifluoromethyl)sulfene adducts, X-ray crystallography[8−10] revealed that the tertiary amines were bound through S−N bonds.[11] In all instances, sulfene−Lewis base adducts were described as colorless solids. In Scaiano's study,[3] on the other hand, sulfene **2** was found to react efficiently with pyridine (k_{py} = $3.9 \cdot 10^6$ $\text{M}^{-1} \cdot \text{s}^{-1}$), yielding an intensely absorbing product (λ_{max} = 440 nm, in acetonitrile), which was assigned as the sulfene pyridine ylide **5**. This implies either that Scaiano's assignment is wrong, or that sulfonyl-substituted sulfene−pyridine adducts such as **5** differ significantly in their natures from all other derivatives studied so far. As this matter should be resolvable by computational chemistry, this study was undertaken. It employs both ab initio and density functional theory.



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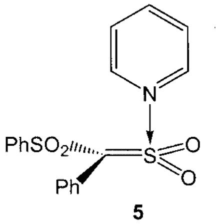

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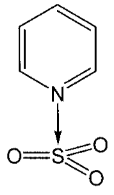

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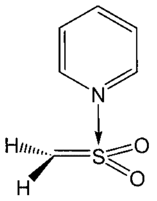

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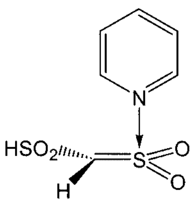

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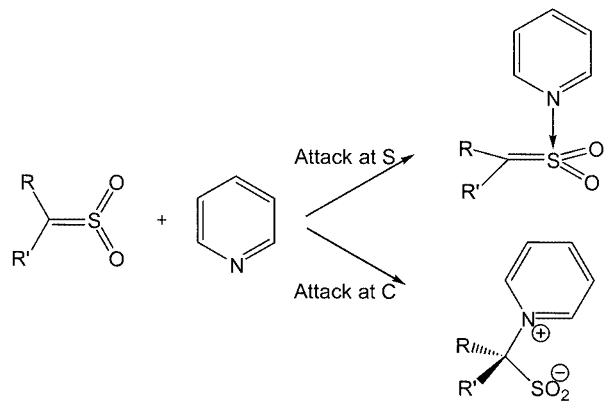
Results and Discussion

Geometries of Pyridine-Sulfene Adducts

Interaction between pyridine and sulfenes may occur at two different sites. Nucleophilic attack of pyridine at the sulfene S results in formation of a S−N bound adduct, which may be regarded either as an ylide or as a Lewis acid/Lewis base complex. Nucleophilic attack of pyridine at the sulfene C, on the other hand, gives a N−C bound adduct, which can be described as a pyridinium-sulfinate zwitterion (Scheme 2).



Scheme 2

Any conclusion regarding the outcome of a reaction between pyridine and sulfene **2** depends on a reliable description of the geometries and the properties of the different types of adducts. In order to evaluate different methods, reference points were needed. The pyridine−SO_3 adduct (py-SO_3) **6** was chosen as one such, as its gas-phase structure has recently been determined.[5] The py-SO_3 adduct **6** has an experimentally measured S−N bond length of 191.5 pm. The experimentally ascertained geometry of py-SO_3 **6** was found to be reproduced reasonably well by second-order Moller−Plesset theory (MP2) with a fairly large aug-cc-pVTZ basis.[5] As this method would have been prohibitively expensive for sulfene **2** and its pyridine adducts, various DFT methods were tested both on py-SO_3 **6** and on the adduct formed between pyridine and the parent sulfene (py-SO_2CH_2, **7**). As further reference points, the geometry calculated for **7** (MP2/aug-cc-pVTZ) and that optimized for model compound **8** (MP2/cc-pVTZ) were chosen. Table 1 summarizes the results of these calculations.

The interaction between pyridine and sulfur trioxide in **6** is predicted to be consistently much stronger than the interaction between pyridine and parent sulfene **7**, as evidenced by the much shorter S−N bond lengths. While **6** is described well by Hartree−Fock theory, the same does not hold for **7**. Of the DFT methods,[11] the B3PW91 and in particular the BHandHLYP hybrid methods give reasonable geometries, while the standard B3LYP method does not perform as well. As the standard 6-31G(d) and the cc-pVTZ basis set give comparable results, BHandHLYP/6-31G(d) was selected as the method of choice for the description of the larger systems of interest to this study. This method also fares well for model compound **8**, for which a geometry optimized at the MP2/cc-pVTZ level of theory could be obtained as a reference point. The geometries both of sulfene adduct **5** and of the model compound **8** ($HSO_2CH=SO_2$ × pyridine) obtained by use of BHandHLYP/6-31G(d) clearly indicate that the S−N bonds in both **5** and **8** should have considerable covalent character. In both cases, r_{S-N} is only slightly longer than in py-SO_3 **6** and significantly shorter than r_{S-N} calculated for py-

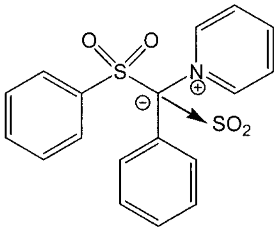
Table 1. Nitrogen−sulfur bond lengths for pyridine−SO_3 (**6**), pyridine−SO_2=CH_2 (**7**), pyridine−SO_2=CH(SO_2H) (**8**), and pyridine−SO_2=CPh(SO_2Ph) (**5**), calculated at various levels of theory (in Angstroms)

Method	R(N−S) Py−SO_3	R(N−S) Py−SO_2CH_2	R(N−S) Py−SO_2CHSO_2H	R(N−S) Py−SO_2CPhSO_2Ph
RHF/6-31G(d)	1.900	2.724	1.915	1.955
MP2/6-31G(d)	2.016	2.435	2.096	2.156
MP2/cc-pVTZ	1.982	2.299	2.035	−
MP2/aug-cc-pVTZ	1.961[a]	2.251	−	−
B3LYP/6-31G(d)	2.036	2.499	2.132	2.233
B3LYP/cc-pVTZ	2.039	2.536	−	−
B3PW91/6-31G(d)	1.991	2.412	2.069	2.136
B3PW91/cc-pVTZ	1.983	2.418	−	−
BHandHLYP/6-31G(d)	1.933	2.450	1.984	2.040
BHandHLYP/cc-pVTZ	1.924	2.492	1.972	−
Exp.	1.915[a]	−	−	−
BHandHLYP/6-31G(d) scipcm (solvent CH_3CN)	−	2.170	1.894	−

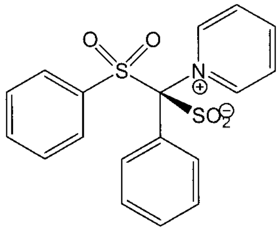
[a] Ref.[5]

SO_2CH_2 **7** at the same level of theory. A comparison of the geometries of **5**, **6**, **7**, and **8** calculated at the B3PW91/6-31G(d) or MP2/6-31G(d) levels of theory suggests the same conclusion. The geometries of Lewis acid/base adducts have been shown to differ significantly between the gas phase and the condensed phase.[12] As adduct **5** was generated in acetonitrile as solvent,[3] the geometries of the model systems **7** and **8** in this particular solvent were calculated by the scipcm method.[13,14] The results, shown in Table 1, indicate that the two model systems are more tightly bound in CH_3CN than they are in the gas phase. For both solvated compounds, the S−N bond is predicted to be significantly contracted, by 5% (**8**) or 12% (**7**). Most probably, the S−N bond will also be contracted in **5**.

An alternative reaction pathway involves attack by pyridine at the sulfene C rather than at the sulfene S atom. This reaction gives species that can be formally described as pyridinium−sulfinate zwitterions. Table 2 lists the calculated C−S bond lengths of the three compounds **9**, **10**, and **11** calculated by a variety of methods. As a reference point, the geometry of **10** was calculated by MP2 theory with a relatively large basis set (cc-pVTZ). A comparison of different methods used to optimize the geometry of **10** reveals that Hartree−Fock theory systematically underestimates R(C-S). Of the DFT methods, B3LYP gives good results. An optimization of **10** by B3PW91/6-31G(d), on the other hand, yielded the structure of the isomer **7**. As a general trend, the calculations indicate that the C−S bond should be significantly longer for the sulfonylated derivatives **11** and **9** than for the parent system **10**. For that reason, the product formed by attack of pyridine at the sulfene C-atom of **2** is probably better described as a Lewis acid/base adduct **9a** between the pyridine ylide of phenyl(phenylsulfonyl)carbene and SO_2 rather than as a pyridinium−sulfinate zwitterion **9b**.



9a



9b

Table 2. Carbon−sulfur bond lengths for pyridine−CH_2SO_2 (**10**), pyridine−CH(SO_2H)SO_2 (**11**), and pyridine−CPh(SO_2Ph)SO_2 (**9**), calculated at various levels of theory (in Angstroms)

Method[a]	R(C−S) Py−CH_2SO_2	R(C−S) Py−CH(SO_2H)SO_2	R(C−S) Py−CPh(SO_2Ph)SO_2
RHF/6-31G(d)	1.881	2.072	2.113
MP2/6-31G(d)	2.061	2.446	2.456
MP2/cc-pVTZ	2.161	−	−
B3LYP/6-31G(d)	2.044	2.324	2.392
B3LYP/cc-pVTZ	2.077	2.390	−
B3PW91/6-31G(d)	a	−	−
BHandHLYP/6-31G(d)	1.947	2.183	2.216
BHandHLYP/cc-pVTZ	1.957	2.235	−
BHandHLYP/6-31G(d) scipcm (solvent CH_3CN)	1.891	2.061	−

[a] Optimized geometry is that of Py-SO_2CH_2 **7**.

As a summary of the results presented so far, it appears that sulfenes can form two types of pyridine adducts. One of these can be described as a Lewis acid/base complex in analogy to pyridine−SO_3 **6**, and it is formed by nucleophilic attack of pyridine at the highly electrophilic sulfene sulfur atom. The presence of a sulfonyl substituent on the sulfene carbon atom makes the sulfene more electrophilic and thus results in stronger binding to pyridine. The other type of adduct can formally be described as a pyridinium−sulfinate zwitterion. It is formed by nucleophilic attack of pyridine at the sulfene carbon atom. The long carbon−sulfur bond lengths calculated for this type of adduct indicate that in the gas phase the zwitterionic description is not correct and that these compounds would probably be better described as Lewis acid/base adducts between sulfur dioxide and the pyridine ylides of methylene (**10**), (phenylsulfonyl)carbene (**11**), or phenyl(phenylsulfonyl)carbene (**9**). Because of the electron-withdrawing effects of the sulfonyl substituents, complexes can be anticipated to be weaker for **9** and **11**. This is consistent with the longer C−S distances calculated in **9** and **11**, in relation to **10** (see Table 2). In acetonitrile solution, both types of adducts are predicted to be bound more tightly.

Time-dependent DFT

In order to identify the species being formed in Scaiano's experiments, the UV/Vis spectra of the N−S bound adduct **5** and the N−C bound adduct **9** were calculated by time-dependent density functional theory [TD-B3LYP/6-31+G(d)],[15,16] based on geometries obtained by BHandHLYP/6-31G(d) for **5** and B3LYP/6-31G(d) for **9**. The longest-wavelength absorption of **5** (λ_{max} = 376.9 nm, f = 0.0512) is found in the UV part of the spectrum, which is not consistent with the λ_{max} = 440 nm of the transient detected in Scaiano's work.[3] For **9**, the same method yielded a λ_{max} = 372.2 with f = 0.1863, which is also far from λ_{max} (exp.) = 440 nm. As the calculated geometries of both species depend strongly on the method used [gas-phase DFT against scipcm(CH_3CN) DFT], the UV/Vis spectra obtained from TD-DFT calculations may also vary significantly with the method used for geometry optimization. In order to check for this possibility, the UV/Vis spectra of the model compounds **7**−**8** and **10**−**11** were calculated by TD-B3LYP/6-31+G(d), based both on calculated gas-phase geometries and on geometries obtained by the scipcm method in acetonitrile as solvent.[17] The results are given in Table 3.

The calculated absorption maxima of **7** and **8** and of **10** and **11**, solvated by acetonitrile, are consistently red-shifted by ca. 60 nm relative to the corresponding absorption maxima of the gas-phase species. Addition of 60 nm to the longest-wavelength λ_{max} values of **5** and **9** brings both of them close to the experimentally measured value of λ_{max} = 440 nm [estimated values: λ_{max} = 437 nm (**5**), 432 nm (**9**)]. Hence, calculation of UV/Vis spectra does not allow for identification of the species formed upon reaction between sulfene **2** and pyridine.

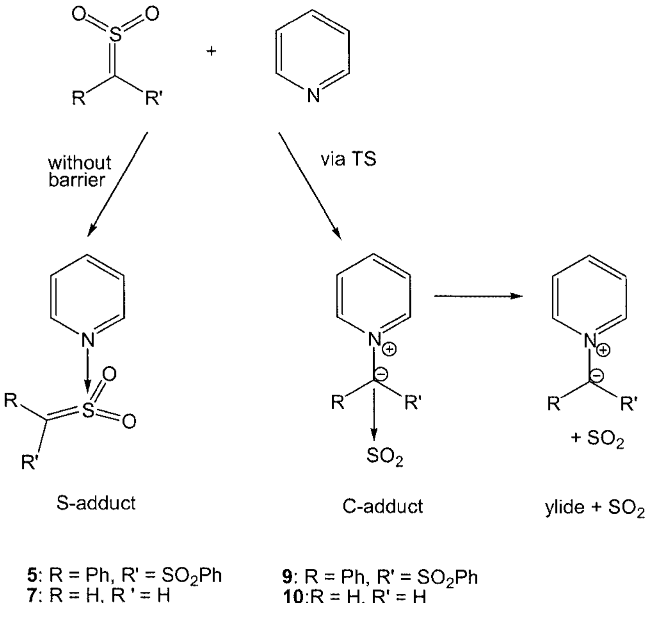
Table 3. Calculated (TD-B3LYP/6-31+G(d)] longest-wavelength absorption maxima of compounds **5** and **7**−**11**; λ_{max} in nm; in brackets: calculated oscillator strength; geometries optimized by BHandHLYP/6-31G(d) for **5** and **7**−**8** (gas phase), by B3LYP/6-31G(d) for **9**−**11** (gas phase), and by scipcm (CH_3CN) BHandHLYP/6-31G(d) for **7**−**8**, **10**−**11**

Compound	gas phase: λ_{max} (osc. strength)	CH_3CN: λ_{max} (osc. strength)
5	376.9 (0.0512)	n.c.[a]
7	269.3 (0.0178)	331.8 (0.0408)
8	330.6 (0.0365)	385.5 (0.0436)
9	372.2 (0.1863)	n.c.
10	380.3 (0.2214)	445.8 (0.1648)
11	354.8 (0.2104)	410.4 (0.1461)

[a] n.c.: not calculated.

Potential Energy Surfaces

The potential energy surfaces for the reactions between parent sulfene $CH_2{=}SO_2$ **12** and phenyl(phenylsulfonyl)sulfene **2** with pyridine (Scheme 3) were calculated by both density functional and MP2 ab initio theory. The B3LYP and BHandHLYP methods were used, with 6-31G(d) and cc-pVTZ basis sets for **12** and a 6-31G(d) basis set for **2**. The results are given in Table 4. The energies are available as supplementary material (Table S1).



Scheme 3

In all cases, attack of pyridine at the sulfene C-atom is predicted to be more exothermic than attack at the sulfene S-atom. The difference is most pronounced in the parent system, for which formation of the Lewis acid/base adduct **7** is calculated (B3LYP/cc-pVTZ) to be only weakly exothermic (by 4.9 kcal/mol), whereas formation of the N−C

Table 4. Enthalpies of activation and reaction enthalpies for sulfene reactions

Method	System[a]	$\Delta H^{\#}$ (*C* adduct)[b]	ΔH (*C* adduct)[b]	ΔH (*S* adduct)[b]	ΔH (ylide)[c]
MP2/cc-pVTZ	Py +12	15.8	−24.6	−9.7	18.9
B3LYP/ 6-31G(d)	Py +12	9.1	−27.9	−6.9	21.5
B3LYP/cc-pVTZ	Py +12	14.1	−21.8	−4.9	18.1
BHandHLYP/6-31G(d)	Py +12	12.6	−27.9	−8.1	28.3
BHandHLYP/ cc-pVTZ	Py +12	18.6	−20.6	−5.8	23.7
B3LYP/6-31G(d)	Py +2	13.5	−23.6	−12.4	9.7
BHandHLYP/ 6-31G(d)	Py +2	16.4	−23.3	−15.7	12.7

[a] Py = pyridine. [b] kcal/mol. [c] Reaction enthalpy for cleavage of the C adduct into a carbene-pyridine ylide and SO_2, in kcal/mol.

bound adduct **10** is predicted to be much more favorable ($\Delta H = -21.8$ kcal/mol). In the case of the phenyl(phenylsulfonyl)-substituted system, attack at carbon is still more favorable than attack at S [B3LYP/6-31G(d): $\Delta H = -12.4$ kcal/mol for S attack against −23.6 kcal/mol for C attack], but the discrepancy is not quite as pronounced.

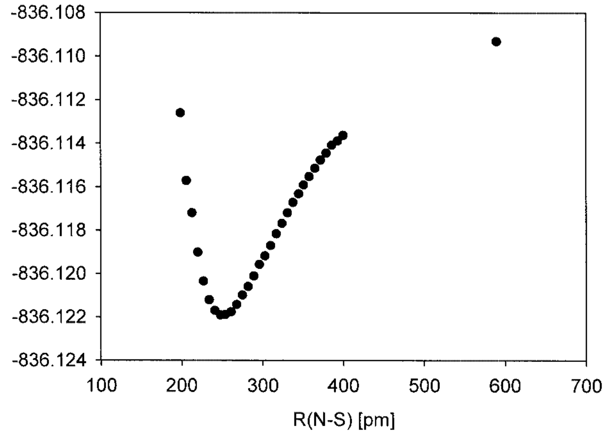


Figure 1. Reaction between parent sulfene **12** and pyridine, S−N adduct formation: plot of the energy in Hartrees, as calculated by B3LYP/6-31G(d), against the sulfur−nitrogen distance; all other geometric parameters were optimized for each value of *R*(S−N); the energy of the separate reactants is given for the arbitrary value of *R*(S−N) = 590 pm

Figure 1 shows that the formation of **7** from pyridine +**12** is calculated to proceed without any barrier. Because of the size of the system, no analogous energy profile for the reaction between **2** and pyridine, yielding **5**, was calculated. Because of the additional sulfonyl substituent, sulfene **2** would be expected to be more electrophilic than **12**. It thus appears very likely that the formation of **5** would also proceed without any barrier.[18] For the formation of C-bound adducts such as **9** and **10**, on the other hand, a significant barrier of the order of 14 kcal/mol has to be overcome. The optimized geometries of the transition states linking (pyridine +**12**) and **10** as well as (pyridine +**2**) and **9** are shown in Figure 2, together with the optimized geometries of adducts **5**, **7**, **9**, and **10**.

The reaction between the pyridine ylide of methylene and SO_2, yielding **10**, was investigated by calculation of an energy profile for the approach of SO_2 [B3LYP/6-31G(d)], as shown in Figure 3.

The energy profile indicates that the reaction proceeds without any significant barrier. For that reason, the reaction between the pyridine ylide of phenyl(phenylsulfonyl)-carbene and SO_2, yielding **9**, would also be expected to proceed with little or no barrier. The formation of **9**/**10** from the sulfenes and pyridine, on the other hand, involves a significant weakening of the C−S bond of the sulfene, as indicated by the rather long C−S bond lengths [MP2/6-31G(d): $r_{C-S} = 245.6$ pm for **9**] in **9**/**10**. This is probably the reason why the formation of **9**/**10** comes with a barrier. Finally, no TSs could be located for a concerted rearrangement of **7** into **10** or of **5** into **9**. Such a TS could only be located with PM3 semiempirical theory, but this result was not confirmed when the TS geometry optimization was repeated with DFT. Conversion of **7** into **10** or of **5** into **9** therefore probably has to proceed through the free sulfenes plus pyridine. Overall, the calculations indicate that the Lewis acid/base adducts **5** and **7** are the products formed in a kinetically controlled reaction, while the "zwitterions" or carbene ylide/SO_2 adducts **9** and **10** are the thermodynamically favored products. MP2 theory confirms this conclusion. The *C*-bound adduct **10** is predicted by MP2/cc-pVTZ to be lower in energy than the *S*-bound adduct **7** by 14.9 kcal/mol. For **5** and **9**, ab initio calculations were performed at the MP2/6-31G(d) level of theory. Here, the energy balance was 18.3 kcal/mol in favor of the *C*-bound adduct **9**.[19]

Conclusion

Reactions between sulfenes and pyridine can yield sulfur-bound adducts, which in the gas phase are best described as typical Lewis acid/Lewis base adducts. In polar solvents such as acetonitrile, these adducts are predicted to show significantly shorter S−N bond lengths and higher degrees of pyramidalization at sulfur. Time-dependent DFT calcu-

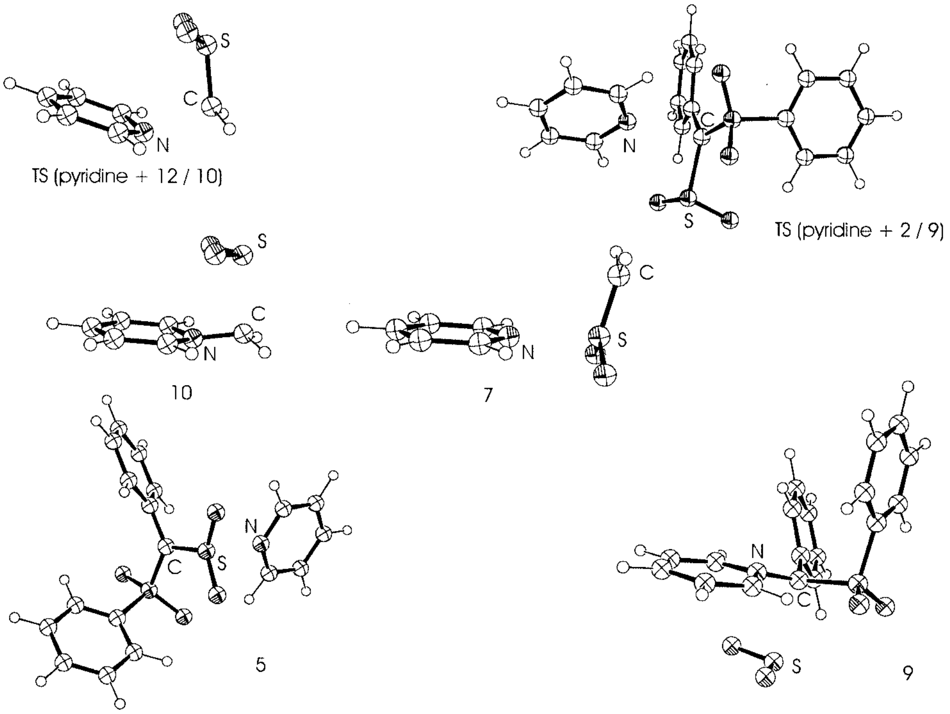


Figure 2. Ortep drawing of the transition structure linking (pyridine +**12**) and **10** (MP2/cc-pVTZ); Ortep drawing of the TS linking (pyridine +**2**) and **9** [B3LYP/6-31G(d)]; Ortep drawings of the sulfene-pyridine adducts **5** and **9** [MP2/6-31G(d)] and **7** and **10** (MP2/cc-pVTZ); the pyridine N and the sulfene S and C are labeled as such

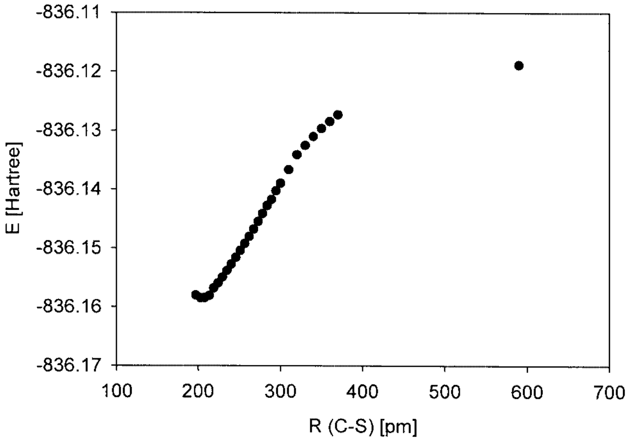


Figure 3. Reaction between the pyridine ylide of methylene (py-CH_2) and SO_2, yielding **10**: plot of the energy in Hartrees, as calculated by B3LYP/6-31G(d), against the sulfur−carbon distance; for each value of R(S−C) all other geometric parameters were optimized; the energy of the separate reactants is given for the arbitrary value of R(S−C) = 590 pm

lations indicate some degree of ylide character (i.e., absorption in the visible range of the spectrum) in polar solvents. Alternatively, carbon-bound adducts may be formed, best described in the gas phase as Lewis acid/Lewis base adducts of SO_2 and carbene-pyridine ylides rather than as pyridinium sulfinate zwitterions. Solvation by polar solvents such as acetonitrile should result in significantly shorter S−C bond lengths and higher degrees of pyramidalization at the ylide carbon. Time-dependent DFT calculations again indicate some degree of ylide character (i.e., absorption in the visible range of the spectrum) in polar solvents. Formation of the *C*-bound adducts is generally predicted to be more exothermic than formation of the S-bound adducts. For C−N bond formation, however, a barrier of at least 14 kcal/mol has to be overcome, while no transition structure is found for S−N adduct formation. The S−N adduct is thus probably formed under conditions of kinetic reaction control (such as laser flash photolysis), while the C−N adducts are the thermodynamically favored products.

Computational Methods

The Gaussian98[20] suite of programs was used for all calculations except for the energy profiles shown in Figures 1 and 3, which were obtained by use of Titan[21] software. All geometries given were fully optimized. When DFT was used, vibrational frequencies were calculated in order to characterize the geometries obtained as stationary points (minima or transition states). All energies given are corrected for zero-point vibrational energy (ZPE). Vibrational analyses, however, were not performed at the MP2 level of theory. Energies obtained by MP2 theory were instead corrected for ZPE as calculated by B3LYP theory. All enthalpies given refer to a temperature of 0 K. TD DFT calculations were performed with TD-B3LYP/6-31+G(d). This approach can be used to calculate solvatochromic effects by inclusion of geometries optimized by the scipcm (Self-Consistent Isodensity Polarized Continuum Model) method.[13]

Supporting Information Available (see also footnote on the first page of this article): Calculated geometries of **5** (MP2/6-31G(d)], **7** (MP2/aug-cc-pVTZ), **8** (MP2/cc-pVTZ), **9** (MP2/6-31G(d)], **10** (MP2/cc-pVTZ), and **11** (MP2/6-31G(d)]. Calculated geometries of the TS linking (pyridine +**12**)/**7** (MP2/cc-pVTZ) and the TS linking (pyridine +**2**)/**6** (B3LYP/6-31G(d)]. Table S1: Energies (in Hartrees) of stationary points relevant to this study, corrected for ZPE.

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[17] *S*-bound adducts **7** and **8**: geometries obtained by BHandHLYP/6-31G[d] and scipcm (CH_3CN) BHandHLYP/6-31G(d). *C*-bound adducts **10** and **11**: geometries obtained by B3LYP/6-31G(d) and scipcm (CH_3CN) BHandHLYP/6-31G(d).

[18] [18a] A transition structure could only be located when the semi-empirical PM3 method was used. Further optimization by B3LYP/6-31G(d), in which no TS was found, indicated that this TS was most probably an artifact of the PM3 method. [18b] The fact that the formation of **5** was reported not to be diffusion-controlled (ref.[3]) may be due to the fact that acetonitrile is a weakly nucleophilic solvent that will probably also coordinate to phenyl(phenylsulfonyl)sulfene **2** and thus has to be replaced by pyridine. The less than diffusion-controlled rate of this reaction reflects the necessity for this replacement.

[19] It should be noted that the ZPE corrections used for these values were calculated by DFT.

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