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Solvation of Sulfur-Centered Cations and Anions in Acetonitrile

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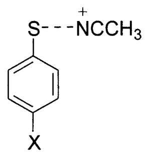
The solvation of substituted phenylsulfenium ions and thiophenoxides in acetonitrile has been analyzed on the basis of experimental and theoretical data. Experimental solvation energies are obtained from previously reported oxidation and reduction potentials of the corresponding arylthiyl radicals in combination with theoretically calculated ionization potentials and electron affinities at the B3LYP/6-31+G(d) level. These calculations provide a consistent set of values in contrast to the data sets obtained in our previous paper (Larsen et al., *J. Am. Chem. Soc.* **2001**, *123*, 1723). The extracted solvation data show the expected substituent dependency for both kinds of ions, i.e., the absolute value of the solvation energy decreases as the charge becomes more delocalized. For the thiophenoxides there is good agreement between the experimental solvation energies and solvation energies computed using the polarizable continuum model (PCM). The solvation of the arylsulfenium ions is much stronger than predicted by the PCM method. This can be attributed to the formation of a strong covalent bond of the Ritter type between the arylsulfenium ion and one molecule of acetonitrile. When this interaction is included in the solvation energy calculations by means of a combined supermolecule and PCM approach the experimental data are reproduced within a few kcal mol^{-1}. While the energy difference of the singlet and triplet spin states of the arylsulfenium ions is almost negligible in gas phase, the singlet cation is undoubtedly the dominating species in solution, since the triplet cation lacks the ability to form a covalent bond with acetonitrile.

Introduction

In a recent paper we reported on the measurement of oxidation and reduction potentials for a series of substituted phenylthiyl radicals, $XC_6H_4S^{\bullet}$.[1] These parameters are important for a deeper understanding of biological systems, atmospheric chemistry and environmental science.[2,3] On the basis of thermochemical cycles in which the measured potentials were combined with theoretically calculated ionization potentials and electron affinities, solvation energies of the pertinent substituted phenylsulfenium ions and thiophenoxides could be extracted. The extracted data showed the expected substituent dependency for both kinds of ions, i.e., the absolute value of the solvation energy decreased as the charge became more delocalized. Interestingly, acetonitrile was found to be better in solvating $XC_6H_4S^+$ than $XC_6H_4S^-$, even though the quantum mechanical calculations of the Mulliken (gas phase) charges showed a substantial charge delocalization in the series of cations. We suggested that the favorable solvation of the cations in acetonitrile might be attributed to a strong specific solvation in terms of the formation of a Ritter-like adduct as depicted in Scheme 1.

SCHEME 1



X = NH_2, OCH_3, CH_3, F, H, Cl, $COOCH_3$, CN, or NO_2

In this paper, our aim is to use quantum chemical calculations to investigate if this suggestion indeed is able to explain the differing solvation behaviors of the two sets of ions or if other kinds of interactions may come into the picture. Our approach will be based on one of the most successful solvation models, the polarizable continuum model (PCM), where the solvent represented by a dielectric continuum is interacting with the charge distribution of the solute.[4−7] The PCM method combines a rigorous quantum chemical description of the molecular charge distribution with a rather flexible approach for defining the solute cavity. This is in contrast to the classical Onsager model in which the solute is represented by a polarizable dipole in a spherical cavity.[8] It is well known that the Onsager model is not capable of predicting reliable solvation energies for complex molecules.[4] On the other hand, using a parameterized description of the solute cavities, it was shown for a set of 28 monovalent ions in water that the PCM method predicts solvation energies with an accuracy close to 1 kcal mol^{-1}.[7] Recently, we have also applied the model successfully in a description of the solvation of both conjugated and nonconjugated carbanions in *N*,*N*-dimethylformamide and tetrahydrofuran.[9] Despite the high accuracy of the PCM method, the computational cost is relatively modest. The time required for computing the wave function of a solvated molecule is only about twice that of computing a gas phase wave function. The major drawback of continuum methods such as PCM is that they cannot account for specific interactions between the solute and solvent mol-

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ecules in the first solvation shell. To investigate the importance of such effects we have also performed quantum chemical calculations on complexes incorporating explicit solvent molecules.

Another point addressed by the present study is the spin state of arylsulfenium ions. It is known from quantum mechanical calculations that the ground state of alkylsulfenium ions is a triplet rather than a singlet, which corresponds to an excited state located at significantly higher energy.[10-12] For arylsulfenium ions, on the other hand, the presence of the adjacent π-system stabilizes the singlet and lowers its energy relative to the triplet. According to a recent ab initio study at the MP2/6-31G(d) level of theory, the singlet state of the phenylsulfenium ion is 15 kcal mol^{-1} lower in energy than the triplet state.[13] However, it is questionable if this computational level is sufficient for an accurate estimate of the singlet−triplet splitting. In this work we have therefore calculated the energy difference using higher levels of theory.

Methods and Procedures

Theoretical Approach. Optimized geometries and harmonic frequencies for all molecules have been computed at the B3LYP/6-31+G(d) level of theory. The B3LYP[14] functional is a modification of the three-parameter exchange-correlation functional of Becke.[15] In addition to the gradient corrected exchange and correlation functionals of Becke[16] and Lee et al.,[17] respectively, it includes a part of the Hartree−Fock exchange energy. Single-point energies were computed at the B3LYP/6-31+G(3df,2p) level of theory using the B3LYP/6-31+G(d) optimized geometries. However, it was found that these calculations gave results only marginally different from the B3LYP/6-31+G(d) energies, and therefore we will report only the latter set of data in this article. Zero point, enthalpy, and free energy corrections to the electronic energies have been calculated based on the unscaled B3LYP/6-31+G(d) frequencies.

With the purpose of investigating the singlet−triplet energy gap of the arylsulfenium ions, we have also performed calculations using the CBS-QB3[18,19] computational scheme. The CBS-QB3 method involves geometry optimization at the B3LYP/6-311(2d,d,p) level and a single point calculation at the CCSD(T)/6-31+G† level. The energy is extrapolated to the infinite basis limit based on the results of MP2 and MP4 calculations with different basis sets. This method also includes empirical corrections for electron pair correlation and spin contamination.

The accuracy of the CBS-QB3 method has been tested on the G2/97[20,21] test set, which is based on 302 experimental energies (heats of formation, ionization potentials, electron affinities, and proton affinities) for molecules containing elements from the first and second chart of the periodic table. The average deviation was found to be 1.10 kcal mol^{-1}, and the maximum deviation 6.2 kcal mol^{-1}.[19] The average deviation of the B3LYP method is 3.29 kcal mol^{-1} when used with the 6-311+G(3df,2p) basis set.[22]

In this study we have also calculated geometries and energies of some molecular complexes at the MP2/6-31+G(d)//MP2/6-31G(d) level of theory. The MP2 method is generally less reliable than the B3LYP method for studying processes that involve the breaking or formation of covalent bonds. On the other hand, MP2 is more accurate than B3LYP for nonbonded interactions, since it provides a proper description of the dispersion component of the interaction energy.

Solvation energies $\Delta G^{\circ}_{\mathrm{sol}}(+)_{\mathrm{PCM}}$, $\Delta G^{\circ}_{\mathrm{sol}}(-)_{\mathrm{PCM}}$, and $\Delta G^{\circ}_{\mathrm{sol}}(\bullet)_{\mathrm{PCM}}$ of the sulfur-centered ions and radicals have been calculated at the B3LYP/6-31G(d) level using the recent implementation of the polarizable continuum model (PCM) in Gaussian 98.[23] The solute cavities in these calculations were made up of overlapping spheres centered at the atomic nuclei. The radii of these spheres were taken as the van der Waals radii of Bondi[24] as implemented in Gaussian 98 and scaled by a factor of 1.2 for all atoms but acidic hydrogens.[23] The solvent parameters, including the dielectric constant, were the same as those implemented for acetonitrile in the program.

To investigate the importance of specific solute−solvent interactions, we have also calculated solvation energies using a supermolecule approach, where we combine an explicit treatment of one or two solvent molecules with the use of the PCM method for estimating the remaining part of the solvation energy. We have previously used this approach successfully to study the catalytic mechanism for hydrolysis of the methyl phosphate anion in aqueous solution.[25] In the present work the same method has been utilized to calculate the change in solvation energy upon addition or removal of an electron to or from the arylthiyl radical. The differentiated solvation energy for the latter process, $\Delta\Delta G^{\circ}_{\mathrm{sol}}(+\bullet)_{\mathrm{sup}}$, is given by eq 1.

$$\begin{aligned}\Delta\Delta G^{\circ}_{\mathrm{sol}}(+\bullet)_{\mathrm{sup}} &\equiv \Delta G^{\circ}_{\mathrm{sol}}(+)_{\mathrm{sup}} - \Delta G^{\circ}_{\mathrm{sol}}(\bullet)_{\mathrm{sup}} \\ &= G(\mathrm{XC_6H_4S^{+}{-}NCCH_3}) + \\ &\quad \Delta G^{\circ}_{\mathrm{sol}}(\mathrm{XC_6H_4S^{+}{-}NCCH_3})_{\mathrm{PCM}} - \\ &\quad G(\mathrm{XC_6H_4S^{\bullet}{-}NCCH_3}) - \\ &\quad \Delta G^{\circ}_{\mathrm{sol}}(\mathrm{XC_6H_4S^{\bullet}{-}NCCH_3})_{\mathrm{PCM}} - \\ &\quad G(\mathrm{XC_6H_4S^{+}}) + G(\mathrm{XC_6H_4S^{\bullet}}) \qquad (1)\end{aligned}$$

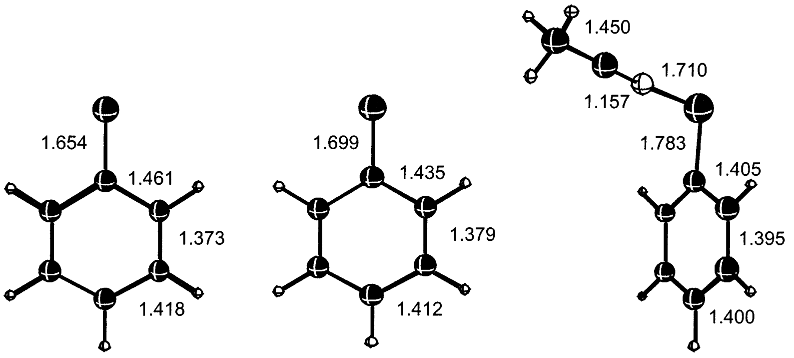
In this expression $G(\mathrm{XC_6H_4S^{+}{-}NCCH_3})$, $G(\mathrm{XC_6H_4S^{\bullet}{-}NCCH_3})$, $G(\mathrm{XC_6H_4S^{+}})$, and $G(\mathrm{XC_6H_4S^{\bullet}})$ are the computed gas phase free energies of the arylsulfenium ion−acetonitrile complex, the arylthiyl radical−acetonitrile complex, the arylsulfenium ion, and the arylthiyl radical, respectively. The parameters $\Delta G^{\circ}_{\mathrm{sol}}(\mathrm{XC_6H_4S^{+}{-}NCCH_3})_{\mathrm{PCM}}$ and $\Delta G^{\circ}_{\mathrm{sol}}(\mathrm{XC_6H_4S^{\bullet}{-}NCCH_3})_{\mathrm{PCM}}$ are the computed PCM solvation energies of the pertinent complexes. It should be noted that this supermolecule approach is not dependent on whether the solute and solvent form a covalent bond. In the case that the solute and solvent are held together by van der Waals interactions, as for the arylthiyl radical−acetonitrile complex, the acetonitrile molecule can be viewed as representing one of the solvent molecules of the first solvation shell. Using an expression analogous to eq 1, $\Delta\Delta G^{\circ}_{\mathrm{sol}}(+\bullet)_{\mathrm{sup}}$ has also been calculated from computational data for a complex containing two molecules of acetonitrile.

In addition, the same type of equation has been used to calculate the solvation free energy change, $\Delta\Delta G^{\circ}_{\mathrm{sol}}(-\bullet)_{\mathrm{sup}}$, associated with adding an electron to the arylthiyl radical, eq 2.

$$\begin{aligned}\Delta\Delta G^{\circ}_{\mathrm{sol}}(-\bullet)_{\mathrm{sup}} &\equiv \Delta G^{\circ}_{\mathrm{sol}}(-)_{\mathrm{sup}} - \Delta G^{\circ}_{\mathrm{sol}}\,(\bullet)_{\mathrm{sup}} \\ &= G(\mathrm{XC_6H_4S^{-}{-}NCCH_3}) + \\ &\quad \Delta G^{\circ}_{\mathrm{sol}}(\mathrm{XC_6H_4S^{-}{-}NCCH_3})_{\mathrm{PCM}} - \\ &\quad G(\mathrm{XC_6H_4S^{\bullet}{-}NCCH_3}) - \\ &\quad \Delta G^{\circ}_{\mathrm{sol}}(\mathrm{XC_6H_4S^{\bullet}{-}NCCH_3})_{\mathrm{PCM}} - \\ &\quad G(\mathrm{XC_6H_4S^{-}}) + G(\mathrm{XC_6H_4S^{\bullet}}) \qquad (2)\end{aligned}$$

In this equation the notation is similar to that of eq 1.

Experimental Approach. The formal relationships used for extracting the two parameters, $\Delta\Delta G^{\circ}_{\mathrm{sol}}(+\bullet)_{\mathrm{exp}}$ and



1 **2** **3**

Figure 1. B3LYP/6-31+G(d) optimized structures of the singlet phenylsulfenium ion (**1**), the triplet phenylsulfenium ion (**2**), and the cation formed between the singlet phenylsulfenium ion and acetonitrile (**3**).

$\Delta\Delta G^\circ_{\rm sol}(-\bullet)_{\rm exp}$, from the experimentally obtained electrode potentials are shown in eqs 3 and 4.[26,27]

$$\Delta\Delta G^\circ_{\rm sol}(+\bullet)_{\rm exp} = -{\rm IP} + FE^\circ_{{\rm XC_6H_4S^+}} + C \qquad (3)$$

$$\Delta\Delta G^\circ_{\rm sol}(-\bullet)_{\rm exp} = {\rm EA} - FE^\circ_{{\rm XC_6H_4S\bullet}} - C \qquad (4)$$

For the constant C a number of 109.3 kcal mol^{-1} is used, which originates from the value of the absolute potential of the standard calomel electrode (= −4.74 V).[28,29] The standard potentials $E^\circ_{{\rm XC_6H_4S^+}}$ and $E^\circ_{{\rm XC_6H_4S\bullet}}$ can be approximated by the half-wave potentials $E^{\rm ox}_{1/2}$ and $E^{\rm red}_{1/2}$, respectively, measured for the radicals by means of photomodulated voltammetry.[1] The ionization potentials, IP, and electron affinities, EA, of the arylthiyl radicals were calculated using the B3LYP/6-31+G(d) approach as already described.

In this context, it is also interesting to have a closer look at the difference of $\Delta\Delta G^\circ_{\rm sol}(+\bullet)_{\rm exp}$ and $\Delta\Delta G^\circ_{\rm sol}(-\bullet)_{\rm exp}$ expressed as the parameter $\Delta\Delta G^\circ_{\rm sol}(\pm)_{\rm exp}$ in eq 5.

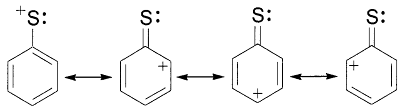
$$\Delta\Delta G^\circ_{\rm sol}(\pm)_{\rm exp} \equiv \Delta\Delta G^\circ_{\rm sol}(+\bullet)_{\rm exp} - \Delta\Delta G^\circ_{\rm sol}(-\bullet)_{\rm exp} = -({\rm IP} + {\rm EA}) + F(E^\circ_{{\rm XC_6H_4S^+}} + E^\circ_{{\rm XC_6H_4S\bullet}}) + 2C \qquad (5)$$

Since the $\Delta\Delta G^\circ_{\rm sol}(\pm)_{\rm exp}$ parameter is independent of the radical species, it describes quite adequately the trend in the solvation characteristics of the ions.

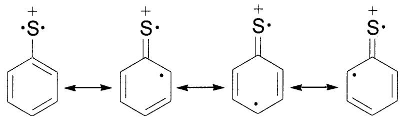
Results and Discussion

Spin States. Before discussing the calculated solvation energies it is important to consider the spin state for arylsulfenium ions. At the B3LYP/6-31+G(d) level the singlet and triplet states of the phenylsulfenium ion are very similar in energy. The singlet state is favored over the triplet state by no more than 0.44 kcal mol^{-1}. This energy difference is reduced to 0.02 kcal mol^{-1} after correction for zero point energies. The energy difference at the zero-point-corrected CBS-QB3 level is 1.53 kcal mol^{-1}. Thus, both computational approaches strongly indicate that the singlet−triplet splitting is very small. This is in contrast to the lower level MP2/6-31G(d) results of Bortolini et al., which showed the singlet state of the phenylsulfenium ion to be 15 kcal mol^{-1} lower in energy than the triplet state.[13] For other systems such as SCNO$^+$ it has been possible to identify both the singlet and triplet cations in gas phase experiments, and in this case the energy difference is 9 kcal mol^{-1}.[30] Although it is hard to make a definite conclusion regarding the spin state of the arylsulfenium ions, it is clear that the singlet state will be strongly stabilized relative to the triplet state, compared to the situation for alkylsulfenium ions. This can be attributed to a significant charge delocalization in the singlet state due to a favorable resonance interaction between the positive sulfur atom and the aromatic ring, as illustrated in Scheme 2.

SCHEME 2



SCHEME 3



The importance of this resonance interaction can be understood from the computed geometry of the singlet phenylsulfenium ion (**1**), which is depicted in Figure 1. The carbon−carbon bonds in the aromatic ring are strongly alternating in length, and the carbon−sulfur bond (1.654 Å) is considerably shorter than a normal single bond (1.81 Å) as predicted from the covalent radii of sulfur and carbon.[31] The charge of the sulfur atom is calculated to be 0.24 au using Mulliken population analysis, which is consistent with the presence of a strong resonance interaction.

The resonance interaction in the triplet state of the phenylsulfenium ion (**2**) differs in character from that in the singlet state. In the triplet state the two lone pair electrons of sulfur are divided upon two p orbitals, where the resonance interaction between the p orbital perpendicular to the plane of the aromatic ring and the aromatic π-system leads to spin delocalization rather than charge delocalization, as illustrated in Scheme 3.

A spin density analysis of the triplet state indicates that approximately half of an unpaired electron is delocalized over the aromatic system with the highest density found at the ortho and para positions. However, the charge delocalization of the singlet state is expected to lead to a larger stabilization than the corresponding spin delocalization of the triplet state. The stronger resonance interaction of the singlet state compared to the triplet state is also confirmed by the more strongly alternating carbon−carbon bond lengths and the shorter carbon−sulfur bond in the former case (see Figure 1). There is also a lower charge on sulfur in the singlet state (0.24 au) than in the triplet state (0.37 au). As we shall see, the magnitude and sign of the

TABLE 1: Half-Wave Potentials $E_{1/2}^{ox}$ and $E_{1/2}^{red}$ Measured by Means of Photomodulated Voltammetry in Acetonitrile along with Calculated Singlet and Triplet Ionization Potentials, IP(S) and IP(T), and Electron Affinities, EA, for $XC_6H_4S^\bullet$

X	$E_{1/2}^{ox}$ [a]	$E_{1/2}^{red}$ [a]	IP(S)[b]	IP(T)[b]	EA[b]
NH_2	0.35	−0.34	7.23	7.66	1.86
OCH_3	0.68	−0.06	7.61	7.94	2.05
CH_3	0.68	0.07	8.06	8.20	2.17
F	0.79	0.15	8.42	8.54	2.37
H	0.79	0.16	8.43[c]	8.44[d]	2.27[e]
Cl	0.90	0.23	8.34	8.45	2.50
$COOCH_3$	0.86	0.43	8.52	8.50	2.77
CN	0.98	0.42	8.88	8.83	3.00
NO_2	f	0.46	9.15	9.02	3.29

[a] In V vs SCE, from ref 1. [b] In eV, calculated at the B3LYP/6-31+G(d) level using the Gaussian 98 suite of programs. [c] The experimental IP is 8.6 ± 0.1 eV and the CBS-QB3 computed value is 8.48 eV. [d] The CBS-QB3 computed IP is 8.55 eV. [e] The experimental EA is 2.26 ± 0.10 eV and the CBS-QB3 computed value is 2.41 eV. [f] No data are available.

singlet−triplet splitting are affected by substituents, which can be explained by considering the substituent effects on the resonance interactions.

IP and EA. In our previous paper[1] the Jaguar program[32] was employed in the calculations, and although it seemed to provide a consistent set of relative results for the series of structurally similar compounds we noted that there were relatively large deviations of the calculated values (IP = 7.98 eV; EA = 2.70 eV) from the experimental ones known in case of the phenylthiyl radical (IP = 8.6 ± 0.1 eV; EA = 2.26 ± 0.10 eV).[33] In the initial phase of this study we redid those calculations at the same level of theory [B3LYP/6-31++G(d,p)] but using the Gaussian 98 software.[23] Rather surprisingly, we found that the results were now in much better agreement with experiment (IP = 8.44 eV; EA = 2.28 eV). A closer examination of the inconsistencies showed that the Jaguar calculation for the phenylthiyl radical converged to an excited state rather than the ground state. Indeed it was possible to get the Gaussian 98 calculation to converge to the same state by swapping the HOMO and LUMO orbitals of β spin and by imposing symmetry in the SCF procedure. We have now recalculated all ionization potentials and electron affinities at a slightly different level of theory [B3LYP/6-31+G(d)], and it is clear that a majority of the earlier results refer to excited states of the arylthiyl radicals. The computed B3LYP/6-31+G(d) IP and EA of the phenylthiyl radical are 8.43 and 2.27 eV, respectively. The corresponding values computed at the CBS-QB3 level of theory are 8.48 and 2.41 eV. Thus, the results from both methods are in reasonable agreement with experiment.

In Table 1 the computed singlet and triplet ionization potentials, IP(S) and IP(T), are listed together with EA. The values of IP(S) show that the resonance donating substituents, NH_2 and OCH_3, have a strongly stabilizing effect on the arylsulfenium ions. There is also a good linear correlation between IP(S) and the σ^+ substituent constant: $\mathrm{IP(S)} = 0.86\sigma^+ + 8.33$, $r^2 = 0.96$. This is not surprising considering that there is through-resonance interaction between the positively charged sulfur and a resonance donating substituent. For triplet state cations such an interaction would be expected to be weaker, and indeed the slope obtained for the linear correlation of IP(T) with σ^+ is smaller: $\mathrm{IP(T)} = 0.60\sigma^+ + 8.42$, $r^2 = 0.93$. Note that while IP(T) is considerably larger than IP(S) for resonance donating substituents there is only a small difference between IP(S) and IP(T) for the electron-withdrawing groups. The latter substituents are known to mediate spin delocalization by resonance interactions, which may explain why their destabilizing effects on the triplet cations are relatively small.[34−36]

The electron affinity of the arylthiyl radicals is strongly affected by the presence of resonance withdrawing substituents such as NO_2 and CN, which is due to a strong through-resonance interaction between the negatively charged sulfur and the substituents on the aromatic ring. Consequently, we also find a linear correlation between EA and σ^-: $\mathrm{EA} = 0.79\sigma^- + 2.25$, $r^2 = 0.93$. This correlation together with that of the IP vs σ^+ relationship show that the substituent effects on IP and EA are dominated by the effects on the charged species rather than on the arylthiyl radicals. This observation stands in sharp contrast to that for the phenoxyl radical system where we have shown earlier that there are considerable substituent effects on the radical stabilization, in particular from resonance donating substituents.[37]

Solvation Energies. In Table 2 the solvation energies $\Delta G^\circ_{sol}(S+)_{PCM}$, $\Delta G^\circ_{sol}(T+)_{PCM}$, $\Delta G^\circ_{sol}(-)_{PCM}$, $\Delta G^\circ_{sol}(\bullet)_{PCM}$, $\Delta\Delta G^\circ_{sol}(+\bullet)_{PCM}$, and $\Delta\Delta G^\circ_{sol}(-\bullet)_{PCM}$ computed by the PCM method are listed together with the corresponding solvation energies, $\Delta\Delta G^\circ_{sol}(+\bullet)_{exp}$, $\Delta\Delta G^\circ_{sol}(-\bullet)_{exp}$, and $\Delta\Delta G^\circ_{sol}(\pm)_{exp}$ obtained from the experimental solution data and computed gas phase data according to eqs 3−5. As the spin state of the sulfenylium ions can be either singlet or triplet, we have included both $\Delta G^\circ_{sol}(S+)_{PCM}$ and $\Delta G^\circ_{sol}(T+)_{PCM}$. In general, the difference between $\Delta G^\circ_{sol}(S+)_{PCM}$ and $\Delta G^\circ_{sol}(T+)_{PCM}$ is small, and in the further treatment of the data we will only employ the $\Delta G^\circ_{sol}(S+)_{PCM}$ data for reasons that will become clear below. Note that the $\Delta\Delta G^\circ_{sol}(+\bullet)_{exp}$ and $\Delta\Delta G^\circ_{sol}(-\bullet)_{exp}$ values differ from those published in our previous paper[1] because of the errors present in the previously employed IP and EA data. The uncertainty on $\Delta\Delta G^\circ_{sol}(+\bullet)_{exp}$ and $\Delta\Delta G^\circ_{sol}(-\bullet)_{exp}$ is estimated to be ±4 kcal mol^{-1}. The calculations of $\Delta G^\circ_{sol}(\bullet)_{PCM}$ show that the solvation of the neutral $XC_6H_4S^\bullet$ species as expected is relatively weak, the only exception being for X = NH_2 with $\Delta G^\circ_{sol}(\bullet)_{PCM} = -6.1$ kcal mol^{-1}. For all substituents but NH_2, the approximations $\Delta\Delta G^\circ_{sol}(+\bullet) \approx \Delta G^\circ_{sol}(+)$, and $\Delta\Delta G^\circ_{sol}(-\bullet) \approx \Delta G^\circ_{sol}(-)$ thus hold. It is not surprising that the NH_2-substituted phenylthiyl radical has the lowest solvation energy of the $XC_6H_4S^\bullet$ species, since this is the only substituent capable of donating hydrogen bonds. However, considering that the aqueous solvation energy of aniline is −4.9 kcal mol^{-1},[7] the solvation of $H_2NC_6H_4S^\bullet$ is stronger than expected.

For the anions, a relatively small but consistent difference of 3−5 kcal mol^{-1} is found between the computed and experimental values of $\Delta\Delta G^\circ_{sol}(-\bullet)$ listed in columns 8 and 9, respectively. This shows that the substituent effects on the two data sets are largely the same as also manifested by the linear relationship obtained between $\Delta\Delta G^\circ_{sol}(-\bullet)_{PCM}$ and $\Delta\Delta G^\circ_{sol}(-\bullet)_{exp}$ in Figure 2. The fact that the PCM method works quite well for the whole series of anions indicates that the solvation energies of the anions are largely determined by the degree of charge delocalization in the system. The $\Delta\Delta G^\circ_{sol}(-\bullet)_{exp}$ values vary from −61 kcal mol^{-1} in the case of X = OCH_3, CH_3, and H to −44 kcal mol^{-1} for X = NO_2. Accordingly we also find a reasonable linear correlation between $\Delta\Delta G^\circ_{sol}(-\bullet)_{exp}$ and the substituent constant σ^-: $\Delta\Delta G^\circ_{sol}(-\bullet)_{exp} = 9.7\sigma^- - 59.0$, $r^2 = 0.90$.

In contrast to this nice consistency in the anion data sets stand the large deviations observed in the two sets of $\Delta\Delta G^\circ_{sol}(+\bullet)$ data; the experimental values (column 7) are found to be not only considerably larger in magnitude than the corresponding computed values (column 6), in some cases by as much as

TABLE 2: Computed Solvation Energies $\Delta G^\circ_{sol}(S+)_{PCM}$, $\Delta G^\circ_{sol}(T+)_{PCM}$, $\Delta G^\circ_{sol}(-)_{PCM}$, $\Delta G^\circ_{sol}(\bullet)_{PCM}$, $\Delta\Delta G^\circ_{sol}(+\bullet)_{PCM}$, and $\Delta\Delta G^\circ_{sol}(-\bullet)_{PCM}$ and Solvation Energies $\Delta\Delta G^\circ_{sol}(+\bullet)_{exp}$, $\Delta\Delta G^\circ_{sol}(-\bullet)_{exp}$, and $\Delta\Delta G^\circ_{sol}(\pm)_{exp}$ Calculated from Experimental Solution Data and Computed Gas Phase Data[a]

X	$\Delta G^\circ_{sol}(S+)_{PCM}$[b]	$\Delta G^\circ_{sol}(T+)_{PCM}$[b]	$\Delta G^\circ_{sol}(-)_{PCM}$[b]	$\Delta G^\circ_{sol}(\bullet)_{PCM}$[b]	$\Delta\Delta G^\circ_{sol}(+\bullet)_{PCM}$[b,c]	$\Delta\Delta G^\circ_{sol}(+\bullet)_{exp}$[d]	$\Delta\Delta G^\circ_{sol}(-\bullet)_{PCM}$[b,e]	$\Delta\Delta G^\circ_{sol}(-\bullet)_{ex}$[f]	$\Delta\Delta G^\circ_{sol}(\pm)_{exp}$[g]
NH_2	−51.0	−46.7	−60.9	−6.1	−44.9	−49	−54.9	−59	11
OCH_3	−41.7	−40.2	−56.1	0.2	−41.9[h]	−51	−56.2	−61	10
CH_3	−42.2	−41.7	−54.7	1.8	−44.0	−61	−56.4	−61	0
F	−46.5	−46.3	−53.9	0.9	−47.4	−67	−54.8	−58	−9
H	−46.0	−45.5	−56.2	0.7	−46.7[i]	−67	−56.9[j]	−61	−6
Cl	−44.6	−44.8	−51.5	1.1	−45.6	−62	−52.6	−57	−5
$COOCH_3$	−41.3	−42.9	−47.8	1.9	−43.2	−67	−49.7	−55	−12
CN	−49.1	−51.0	−47.4	−0.7	−48.4[k]	−73	−46.6	−50	−23
NO_2	−50.4	−52.7	−44.4	0.0	−50.4		−44.3	−44	

[a] All values are in kcal mol^{-1}. [b] Calculated at the PCM-B3LYP/6-31+G(d) level. [c] $\Delta\Delta G^\circ_{sol}(+\bullet)_{PCM} = \Delta G^\circ_{sol}(S+)_{PCM} - \Delta G^\circ_{sol}(\bullet)_{PCM}$. [d] From eq 3. [e] $\Delta\Delta G^\circ_{sol}(-\bullet)_{PCM} = \Delta G^\circ_{sol}(-)_{PCM} - \Delta G^\circ_{sol}(\bullet)_{PCM}$. [f] From eq 4. [g] From eq 5. [h] $\Delta\Delta G^\circ_{sol}(+\bullet)_{sup} = -46.9$ kcal mol^{-1}. [i] $\Delta\Delta G^\circ_{sol}(+\bullet)_{sup} = -68.2$ kcal mol^{-1}. [j] $\Delta\Delta G^\circ_{sol}(-\bullet)_{sup} = -57.0$ kcal mol^{-1}. [k] $\Delta\Delta G^\circ_{sol}(+\bullet)_{sup} = -77.1$ kcal mol^{-1}.

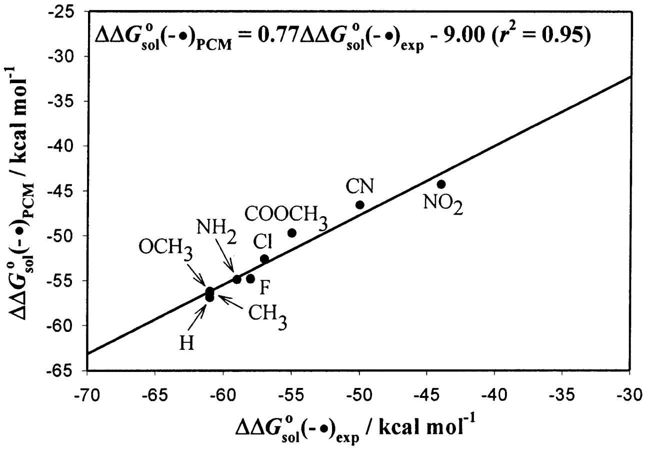


Figure 2. Plot of $\Delta\Delta G^\circ_{sol}(-\bullet)_{PCM}$ against $\Delta\Delta G^\circ_{sol}(-\bullet)_{exp}$.

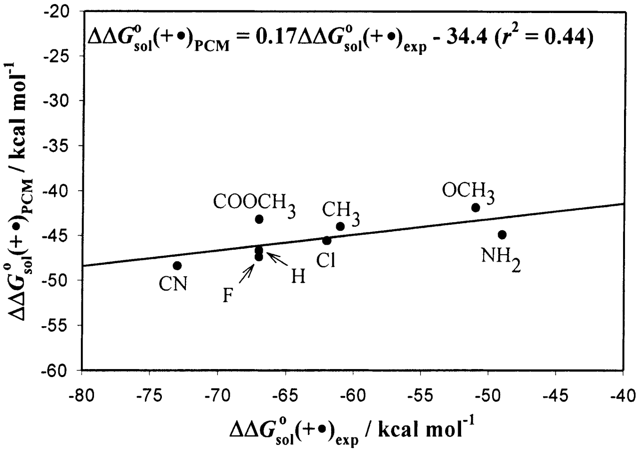


Figure 3. Plot of $\Delta\Delta G^\circ_{sol}(+\bullet)_{PCM}$ against $\Delta\Delta G^\circ_{sol}(+\bullet)_{exp}$.

25 kcal mol^{-1}, but also they exhibit a much larger substituent effect as clearly illustrated by the plot of the two data set in Figure 3. The decrease in the $\Delta\Delta G^\circ_{sol}(+\bullet)_{exp}$ values amounts to 24 kcal mol^{-1} as the degree of charge localization in the cations increases going from X = NH_2 to X = CN. The following correlation with the σ^+ substituent constant is obtained: $\Delta\Delta G^\circ_{sol}(+\bullet)_{exp} = -12.1\sigma^+ - 63.9$, $r^2 = 0.88$. In general, $\Delta\Delta G^\circ_{sol}(+\bullet)_{exp}$ is smaller than $\Delta\Delta G^\circ_{sol}(-\bullet)_{exp}$, indicating that the solvation of the cations is stronger than of the anions. The variation in $\Delta\Delta G^\circ_{sol}(\pm)_{exp}$ listed in the last column of Table 2 is from −23 kcal mol^{-1} for X = CN to 11 kcal mol^{-1} for X = NH_2.[38] In the case of the phenylsulfenium ion with a calculated Mulliken charge of only 0.24 au on the sulfur atom, the $\Delta\Delta G^\circ_{sol}(+\bullet)_{exp}$ value of −67 kcal mol^{-1} is even close to the −71 kcal mol^{-1} found for the solvation energy of the completely localized and smaller potassium ion in acetonitrile.[39]

The above results show that while the PCM approach is sufficiently adequate in the description of sulfur-centered anions, the solvation behavior of the corresponding cations clearly cannot be explained from electrostatic considerations alone. As suggested in our previous paper,[1] the origin of the strong solvation of sulfenylium ions might be specific solvent effects in terms of covalent interactions between the arylsulfenium ions and one or more acetonitrile molecules of the first solvation shell. Actually, in another study it has been shown on the basis of ab initio calculations and mass spectrometry measurements that the phenylsulfenium ion can form strong covalent bonds with molecules such as ethylene and carbon monoxide.[13] In the present work we therefore decided to carry out high-level calculations of the Ritter-like adduct presented in Scheme 1.

The optimized molecular geometry of the singlet phenylsulfenium ion−acetonitrile complex (**3**) is shown in Figure 1. At the B3LYP/6-31+G(d) level the computed gas phase enthalpy and free energy of binding are −28.5 and −21.6 kcal mol^{-1}, respectively. The covalent character of the complex is confirmed by the fact that the S−N bond length of 1.710 Å is close to the 1.74 Å predicted for a typical S−N single bond from the covalent radii of sulfur and nitrogen.[31] A MP2/6-31+G(d)//MP2/6-31G(d) calculation gave a similar geometry with a S−N bond length of 1.710 Å, and only a slightly more negative binding enthalpy of −32.5 kcal mol^{-1}. The S−N bond lies in a plane perpendicular to the aromatic ring at an angle close to 90°. In contrast to the finding for the isolated singlet phenylsulfenium ion (**1**), the aromatic C−C bonds in **3** are almost identical in length. At the same time the C−S bond of **3** is longer than that of **1**. These factors together indicate that the resonance interaction between the aromatic π system and the sulfur atom is essentially lost when the phenylsulfenium ion interacts with acetonitrile. Furthermore, the geometry of the acetonitrile moiety of **3** is almost identical to the geometry of the free acetonitrile molecule. The conclusion must therefore be that the S−N bond is essentially a sigma bond arising from the interaction of an empty p orbital on sulfur, which lies perpendicular to the plane of the aromatic ring, and the nitrogen lone-pair orbital of acetonitrile. The bond is rather polar, since the Mulliken population analysis shows that only 0.32 of an electron has been transferred from the acetonitrile moiety to the phenylsulfenium ion.

The interaction between the triplet phenylsulfenium ion (**2**) and an acetonitrile molecule would be expected to be weaker, since the triplet cation with its two unpaired electrons on sulfur has no empty p orbital that can form a covalent bond with the nitrogen lone-pair orbital. This was indeed confirmed by

B3LYP/6-31+G(d) calculations, which were unable to find a minimum for a covalent bond formation. Instead we found a strong van der Waals complex with a S−N bond length of 2.65 Å and a complexation enthalpy of −9.4 kcal mol^{-1}.

Another possible interaction to consider is the covalent binding of a second molecule of acetonitrile to **3**. However, our calculations at the B3LYP/6-31+G(d) level show that the second acetonitrile molecule binds noncovalently with a S−N bond length of 2.65 Å and a complexation enthalpy of −9.9 kcal mol^{-1}. Calculations at the MP2/6-31+G(d)//MP2/6-31G(d) level gave a slightly shorter and stronger bond with a bond length and complexation enthalpy of 2.51 Å and −14.1 kcal mol^{-1}, respectively.

We also investigated the substituent effect on the bond strength and the geometry of **3**. The resonance donating substituent, OCH_3, weakens the interaction between the singlet arylsulfenium ion and acetonitrile, so that the enthalpy of binding becomes −14.2 kcal mol^{-1}. The S−N bond is also lengthened compared to the unsubstituted case, but it is still sufficiently short, 1.74 Å, to indicate that it is covalent in character. Resonance withdrawing substituents, on the other hand, are found to strengthen the covalent bond. For $X = NO_2$ and CN, the enthalpies of binding are −39.6 and −34.6 kcal mol^{-1}, respectively. In contrast, these substituents exert relatively small effects on the S−N bond length, which is lowered by less than 0.01 Å compared to that of **3**. The large substituent effect on the enthalpy of binding confirms the polar character of the S−N bond; the bond strength is largely determined by the ability of the substituent to donate or withdraw electrons from sulfur. This effect is also in agreement with the large substituent effect on the solvation energies of the cations that was indicated by the experimental measurements.

To estimate if the experimental solvation energies of the cations indeed can be explained by the formation of a covalent bond between the singlet arylsulfenium ion and acetonitrile, we decided to calculate $\Delta\Delta G^{\circ}_{sol}(+\bullet)_{sup}$ and $\Delta\Delta G^{\circ}_{sol}(-\bullet)_{sup}$ values for such ions using the combined supermolecular and PCM approach described in the Methods and Procedure section (see eqs 1 and 2). In the case of X = H, the computed $\Delta\Delta G^{\circ}_{sol}(+\bullet)_{sup}$ value is −68.2 kcal mol^{-1}, meaning that the absolute value of the solvation energy is increased by 21.5 kcal mol^{-1} when compared with $\Delta\Delta G^{\circ}_{sol}(+\bullet)_{PCM} = -46.7$ kcal mol^{-1}. The former value is very close to the corresponding $\Delta\Delta G^{\circ}_{sol}(+\bullet)_{exp}$ value of −67 kcal mol^{-1}. The introduction of a second molecule of acetonitrile leads only to a small decrease in the solvation energy affording $\Delta\Delta G^{\circ}_{sol}(+\bullet)_{sup} = -70.5$ kcal mol^{-1}. For the triplet phenylsulfenium ion, which forms a strong van der Waals complex with acetonitrile, we found that $\Delta\Delta G^{\circ}_{sol}(+\bullet)_{sup} = -50.2$ kcal mol^{-1}, a result comparable with $\Delta\Delta G^{\circ}_{sol}(+\bullet)_{PCM}$ but almost 17 kcal mol^{-1} above $\Delta\Delta G^{\circ}_{sol}(+\bullet)_{exp}$.

We also tested the ability of the supermolecule approach involving one solvent molecule to reproduce the substituent effects on $\Delta\Delta G^{\circ}_{sol}(+\bullet)_{exp}$. For $X = OCH_3$ the $\Delta\Delta G^{\circ}_{sol}(+\bullet)_{sup}$ value was computed to be −46.9 kcal mol^{-1} for the singlet ion, which is in relatively good agreement with the experimental value of −51 kcal mol^{-1}. Also for X = CN the agreement between theory and experiment is satisfactory; the computed and experimental $\Delta\Delta G^{\circ}_{sol}(+\bullet)$ values are −77.1 and −73 kcal mol^{-1}, respectively.

The supermolecule approach is thus able to reproduce the large solvation effects observed experimentally for the cations. To further test the approach, the $\Delta\Delta G^{\circ}_{sol}(-\bullet)_{sup}$ value was also calculated for X = H. This resulted in a solvation energy of −57.0 kcal mol^{-1}, which is almost identical to the pure PCM result of −56.9 kcal mol^{-1} and accordingly also close to the experimental value of −61 kcal mol^{-1}. Thus, the computational method seems to provide reliable solvation energies. The conclusion must therefore be that the high absolute solvation energy of the arylsulfenium ion in acetonitrile can be attributed to the formation of a covalent bond between the singlet cation and one solvent molecule.

Conclusion

The solvation features of substituted phenylsulfenium ions and thiophenoxides in the solvent acetonitrile have been studied on the basis of experimental and theoretical data. Experimental solvation energies are obtained from previously reported oxidation and reduction potentials of the corresponding arylthiyl radicals in combination with theoretically calculated ionization potentials and electron affinities at the B3LYP/6-31+G(d) level. These calculations provide a consistent set of values in contrast to the data sets obtained in our previous paper,[1] where some of the data now are shown to refer to an excited state rather than the ground state. The extracted solvation data show the expected substituent dependency for both kinds of ions, i.e., the absolute value of the solvation energy decreases as the charge becomes more delocalized. The new set of data has been used in a thorough test of one of the most successful solvation models, the polarizable continuum model, where the solvent is treated as a continuum described solely by its dielectric constant. For all anions, the agreement between the quantum chemically calculated and experimental solvation energies is found to be good, independent of the extent of charge localization. On the other hand, the solvation of the cations is much stronger than the PCM method would predict. This we attribute to the fact that the model does not take into account specific solvent effects in terms of strong interactions occurring in the inner solvation shell. We have found that a strong covalent bond can be formed between the singlet state arylsulfenium ion and one molecule of acetonitrile. The gas phase enthalpy of binding for the phenylsulfenium ion is −28.5 kcal mol^{-1}. In addition, there are large substituent effects on the binding enthalpies, which is in line with the trend observed in the experimental solvation energies. Indeed, when the bond formation between the arylsulfenium ions and acetonitrile is included in the solvation energy calculations by means of a combined supermolecule and PCM approach, the experimental data may be reproduced within a few kcal mol^{-1}. While the energy difference of the singlet and triplet spin state of the arylsulfenium ions is almost negligible for the gas phase structures, the singlet state cation is undoubtedly the dominating species in solution, since the triplet state lacks the ability to form a covalent bond.

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