

# Substituent Effects on the Oxidation and Reduction Potentials of Phenylthiyl Radicals in Acetonitrile

Allan Godsk Larsen, Allan Hjarbæk Holm, Mark Roberson, and Kim Daasbjerg\*

Contribution from the Department of Chemistry, University of Aarhus, Langelandsgade 140, DK-8000 Aarhus C, Denmark

Received October 30, 2000. Revised Manuscript Received December 14, 2000

**Abstract:** Oxidation ( $E_{1/2}^{\text{ox}}$ ) and reduction potentials ( $E_{1/2}^{\text{red}}$ ) of a series of para-substituted phenylthiyl radicals  $\text{XC}_6\text{H}_4\text{S}^\bullet$  generated from the pertinent disulfides or thiophenols have been measured by means of photomodulated voltammetry in acetonitrile. The values of  $E_{1/2}^{\text{ox}}$  are of particular interest as they give access to the hitherto unknown thermochemistry of short-lived phenylsulfenium cations in solution. Both  $E_{1/2}^{\text{ox}}$  and  $E_{1/2}^{\text{red}}$  decrease as the electron-donating power of the substituent raises, resulting in linear correlations with the Hammett substituent coefficient  $\sigma^+$  with slopes  $\rho^+$  of 4.7 and 6.4, respectively. The finding of a larger substituent effect on  $E_{1/2}^{\text{red}}$  than  $E_{1/2}^{\text{ox}}$  is a consequence of a corresponding development in the electron affinities and ionization potentials of  $\text{XC}_6\text{H}_4\text{S}^\bullet$  as revealed by quantum-chemical calculations. Solvation energies extracted for  $\text{XC}_6\text{H}_4\text{S}^+$  and  $\text{XC}_6\text{H}_4\text{S}^-$  from thermochemical cycles show the expected substituent dependency; i.e., the absolute values of the solvation energies decrease as the charge becomes more delocalized in the ions. Acetonitrile is better in solvating  $\text{XC}_6\text{H}_4\text{S}^+$  than  $\text{XC}_6\text{H}_4\text{S}^-$  for most substituents, even if there is a substantial delocalization of the charge in the series of phenylsulfenium cations. The substituent effect on  $E_{1/2}^{\text{red}}$  is smaller in aqueous solution than acetonitrile, which is attributed to the ability of water to stabilize in particular localized anions through hydrogen bonding.

## Introduction

The important role of sulfur compounds and in particular sulfur-centered radicals in biological systems, atmospheric chemistry, and environmental science is now well established.<sup>1,2</sup> As a consequence, much attention has been paid to the thermochemistry of these species. Techniques such as calorimetry, mass spectrometry, laser photodetachment, electrochemistry, and pulse radiolysis have provided a wealth of gas-phase and solution data in terms of heats of combustion and formation, bond dissociation energies, electron affinities, ionization potentials, and reduction potentials. Extensive compilations containing critical examinations of these data are available in the literature.<sup>3–7</sup>

Despite the intensive research in the chemistry of sulfur compounds, no reports have appeared so far on the thermochemistry of sulfenium cations  $\text{RS}^+$  in solution. Sulfenium cations have often been invoked as intermediates in reaction mechanisms<sup>8–12</sup> even if serious doubts have been advanced of their very existence in condensed phase.<sup>13–16</sup> Because of their

strong electrophilic properties they are most likely associated with nucleophiles (possibly the solvent itself) present in solution. A number of sulfenium cation carriers are therefore known with sulfenyl chloride,  $\text{RSCl}$ , probably being the most prominent species.<sup>17,18</sup> In the gas phase, the situation is less complex and here  $\text{RS}^+$  or, in the case of most alkylsulfenium cations, rather the rearranged  $\text{R}(-\text{H})=\text{SH}^+$  has been detected in experimental studies.<sup>19–22</sup> Obviously, a similar 1,2-H shift would be impossible for arylsulfenium cations.<sup>23</sup> Quantum-mechanical calculations have shown that the ground state of alkylsulfenium cations

\* Corresponding author: (fax) +4586196199; (e-mail) kdaa@kemi.aau.dk.

(1) *Sulfur-Centered Reactive Intermediates in Chemistry and Biology*; Chatgililoglu, C., Asmus, K.-D., Eds.; NATO ASI Series; Plenum Press: New York, 1990.

(2) *S-centered Radicals*; Alfassi, Z. B., Ed.; John Wiley: Chichester, 1999.

(3) Benson, S. W. *Chem. Rev.* **1978**, *78*, 23.

(4) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. 2.

(5) Griller, D.; Martinho Simões, J. A. M.; Wayner, D. D. M. In *Sulfur-Centered Reactive Intermediates in Chemistry and Biology*; Chatgililoglu, C., Asmus, K.-D., Eds.; NATO ASI Series; Plenum Press: New York, 1990; Chapter 6.

(6) Armstrong, D. A. In *S-centered Radicals*; Alfassi, Z. B., Ed.; John Wiley: Chichester, 1999.

(7) NIST Standard Reference Database No. 69.

(8) Kharasch, N.; Buess, C. M.; King, W. *J. Am. Chem. Soc.* **1953**, *75*, 6035.

(9) Smit, W. A.; Krimer, M. Z.; Vorobieva, E. A. *Tetrahedron Lett.* **1975**, 2451.

(10) Rasteikiene, L.; Greiciute, D.; Linikova, M. G.; Knunyants, I. L. *Russ. Chem. Rev. (Engl. Transl.)* **1977**, *46*, 548.

(11) Bewick, A.; Coe, D. E.; Libert, M.; Mellor, J. M. *J. Electroanal. Chem.* **1983**, *144*, 235.

(12) Boryczka, S.; Elothmani, D.; Do, Q. T.; Simonet, J.; Le Guillanton, G. *J. Electrochem. Soc.* **1996**, *143*, 4027.

(13) Robinson, E. A.; Zaidi, S. A. A. *Can. J. Chem.* **1968**, *46*, 3927.

(14) Capozzi, G.; Lucchini, V.; Modena, G.; Rivetti, F. *J. Chem. Soc., Perkin Trans. 2* **1975**, 361.

(15) Capozzi, G.; Lucchini, V.; Modena, G.; Rivetti, F. *J. Chem. Soc., Perkin Trans. 2* **1975**, 900.

(16) Takeuchi, H.; Hiyama, T.; Kamai, N.; Ōya, H. *J. Chem. Soc., Perkin Trans. 2* **1997**, 2301.

(17) Capozzi, G.; Modena, G.; Pasquato, L. In *The chemistry of sulphenic acids and their derivatives*; Patai, S., Ed.; John Wiley: Chichester, 1990.

(18) Fachini, M.; Lucchini, V.; Modena, G.; Pasi, M.; Pasquato, L. *J. Am. Chem. Soc.* **1999**, *121*, 3944.

(19) Dill, J. D.; McLafferty, F. W. *J. Am. Chem. Soc.* **1979**, *101*, 6526.

(20) Cooks, R. G.; Mabud, Md. A.; Horning, S. R.; Jiang, X.-Y.; Paradisi, C.; Traldi, P. *J. Am. Chem. Soc.* **1989**, *111*, 859.

(21) Ruscic, B.; Berkowitz, J. *J. Chem. Phys.* **1992**, *97*, 1818.

(22) Nourbakhsh, S.; Norwood, K.; He, G.-Z.; Ng, C. Y. *J. Am. Chem. Soc.* **1991**, *113*, 6311.

(23) Paradisi, C.; Hamdan, M.; Traldi, P. *Org. Mass. Spectrom.* **1990**, *25*, 296.

is a triplet rather than a singlet, which corresponds to an excited state located at significantly higher energy.<sup>24–26</sup> The situation is different for arylsulfenium cations, since the presence of the adjacent  $\pi$  system stabilizes the ion and lowers the energy of the singlet state below that of the triplet. According to a recent ab initio study, the energy difference between the two states is 15 kcal mol<sup>-1</sup>.<sup>27</sup>

In this paper, we report on the electrochemical properties of the RS<sup>+</sup>/RS<sup>•</sup> and RS<sup>•</sup>/RS<sup>-</sup> couples in acetonitrile, i.e., the reduction potentials of RS<sup>+</sup> and RS<sup>•</sup>. For the first time, it has been possible to obtain thermodynamic information about a series of para-substituted phenylsulfenium cations, XC<sub>6</sub>H<sub>4</sub>S<sup>+</sup>, in solution by employing the technique of photomodulated voltammetry developed by Wayner and Griller some 10–15 years ago.<sup>28</sup> As this technique also gives access to the reduction potentials of the substituted phenylthiyl radicals, XC<sub>6</sub>H<sub>4</sub>S<sup>•</sup>, and some of these potentials already have been determined in the literature by other methods, the reliability of the experimental procedure employed herein can be checked. Furthermore, by combining the electrode potentials with calculated ionization potentials and electron affinities of the thiyl radicals it becomes possible to extract solvation data for the sulfur-centered cations and anions. The trend in these results will be discussed.

## Experimental Section

**Materials.** Bis(4-aminophenyl), bis(4-methoxyphenyl), bis(4-methylphenyl), diphenyl, bis(4-chlorophenyl), and bis(4-nitrophenyl) disulfide, 4-methoxythiophenol, thiophenol, 4-chlorothiophenol, and 4-nitrothiophenol were obtained commercially from Lancaster or Aldrich. All compounds were used without further purification, the exception being bis(4-nitrophenyl) disulfide, which was recrystallized from acetic acid. Bis(4-cyanophenyl),<sup>29</sup> bis(4-fluorophenyl),<sup>30</sup> and bis-(4-carbomethoxyphenyl) disulfide<sup>31</sup> as well as phenylsulfenyl chloride<sup>32</sup> were prepared and purified according to the procedures outlined in the references cited. Acetonitrile was obtained from Lab-Scan and dried through a column of freshly activated alumina. The supporting electrolyte, tetrabutylammonium tetrafluoroborate (Bu<sub>4</sub>NBF<sub>4</sub>), was prepared and purified by standard procedures.

**Apparatus.** The electrochemical flow cell used in the photomodulated voltammetry technique was a modified version of the cell described in ref 28. It was constructed from Teflon with the actual chamber of the cell having a volume of 380  $\mu$ L (cylindrical:  $\phi = 9$  mm,  $l = 6$  mm) and an inlet and outlet with  $\phi = 1$  mm. The working electrode (gold minigrid, 1000 mesh; platinum minigrid, 250 mesh; carbon fibers worn as a net) was sealed in plastic by heating the plastic to 110 °C. This laminated net functioned as one of the circular walls of the electrochemical cell, and the presence of a hole in the center of the plastic with  $\phi = 5$  mm provided contact between the net and the solution. A cylindrical piece of quartz and an O-ring (EPDM) were placed upon the electrode, and all the parts were firmly fastened with a screw. The quartz piece served as a window for the photolyzing beam. Electrical contact to the working electrode was made with a platinum wire going through the Teflon and plastic. It was constructed so the wire would not be in contact with the solution. The reference electrode was a Flex-Ref electrode (Ag wire in a saturated KCl solution, World Precision Instruments), and it was placed with the tip positioned at the

vicinity of the net in order to diminish the ohmic drop as much as possible. The ohmic drop was compensated by a positive feedback system incorporated in the home-built potentiostat. The counter electrode was another platinum wire located in the exit tube so that products formed at the electrode did not interfere with the measurements. The light source was a 250-W Hg/Xe horizontal lamp (LPS-250, Photon Technology International). The light passed a water filter and was modulated with a light chopper (651, EG&G Instruments). The lamp, filter, chopper, electrochemical cell, and potentiostat were placed on an optical bench. The ac component of the current output from the potentiostat was measured with a lock-in amplifier (SR810 DSP, Stanford Research Systems). All equipment was controlled by means of a PC.

**Procedure.** The main approach employed for generating substituted phenylthiyl radicals consisted of photolyzing aromatic disulfides as shown in eq 1. The concentration of the disulfides was typically 10–



20 mM. This method was supplemented by another well-known procedure, in which di-*tert*-butyl peroxide (10 vol % in acetonitrile) is cleaved homolytically to *tert*-butoxyl radicals, eq 2, which subsequently may abstract a hydrogen atom from XC<sub>6</sub>H<sub>4</sub>SH (concentration  $\approx 3$  mM) in a fast reaction, eq 3. A third procedure was considered in the case



of X = H, in which phenylsulfenyl chloride, C<sub>6</sub>H<sub>5</sub>SCl, was the starting point as shown in eq 4. An output of 70–100 W from the lamp was



sufficient for photolyzing the different substrates. The acetonitrile solution was flowed through the cell with a rate of 2–3 mL min<sup>-1</sup>, and under these circumstances, the temperature near the electrode surface was measured to be 24–26 °C. The frequency of the light chopper was usually 134 Hz. The sweep rate employed was 0.1 V s<sup>-1</sup>. In most cases, the oxidation and reduction processes of the thiyl radicals were studied separately in order to optimize the current signals in the potential range of each process. All potentials were measured relative to the ferrocenium/ferrocene (fc<sup>+</sup>/fc) redox couple and converted to SCE. In a series of measurements of the potential of fc<sup>+</sup>/fc against SCE, we found it to be 0.41 V in acetonitrile.<sup>33</sup> All solutions were deaerated with argon.

Density functional theory calculations were performed using the Jaguar program, version 4.0, release 23.<sup>34</sup> The B3LYP gradient-corrected exchange-correlation functional was used in all cases. The 6-31G\*\* basis set was used in the calculation of Mulliken populations, with diffuse functions added only to the sulfur atom. This gave the basis set the flexibility to handle the buildup of negative charge on that atom in the anion, while avoiding the well-known instability of Mulliken population calculations in the presence of large numbers of diffuse functions.<sup>35</sup> The 6-31++G\*\* basis set was used in the calculation of the adiabatic ionization potentials and electron affinities. All structures were optimized for each basis set, and the Hessians were computed to confirm that the structures were indeed stable points on the potential energy surface.

## Results and Discussion

**Half-Wave Potentials.** Figure 1 shows the photomodulated voltammogram of C<sub>6</sub>H<sub>5</sub>S<sup>•</sup>, generated from photolysis of diphenyl

(24) Rodriguez, C. F.; Hopkinson, A. C. *J. Mol. Struct. (THEOCHEM)* **1987**, 152, 55.

(25) Pople, J. A.; Curtiss, L. A. *J. Phys. Chem.* **1987**, 91, 3637.

(26) Curtiss, L. A.; Nobes, R. H.; Poble, J. A.; Radom, L. *J. Chem. Phys.* **1992**, 97, 6766.

(27) Bortolini, O.; Guerrini, A.; Lucchini, V.; Modena, G.; Pasquato, L. *Tetrahedron Lett.* **1999**, 40, 6073.

(28) Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* **1988**, 110, 132.

(29) Krishnamurthy, S.; Aimino, D. *J. Org. Chem.* **1989**, 54, 4458.

(30) McKillop, A.; Koyunçu, D.; Krief, A.; Dumont, W.; Renier, P.; Trabelsi, M. *Tetrahedron Lett.* **1990**, 31, 5007.

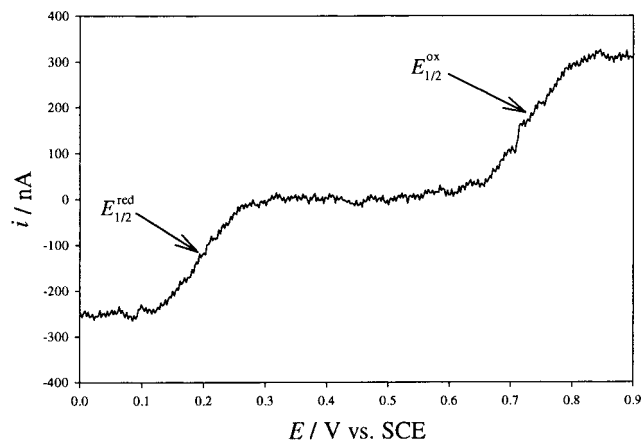
(31) Schuetz, R. D.; Baldwin, R. A. *J. Org. Chem.* **1962**, 27, 2841.

(32) Theobald, P. G.; Okamura, W. H. *J. Org. Chem.* **1990**, 55, 741.

(33) Daasbjerg, K.; Pedersen, S. U.; Lund, H. In *General Aspects of the Chemistry of Radicals*; Alfassi, Z. B., Ed.; John Wiley: Chichester, 1999; Chapter 12, p 410.

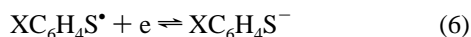
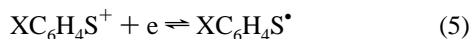
(34) Jaguar 4.0, Schrodinger, Inc., Portland, OR, 2000.

(35) Jensen, F. *Introduction to Computational Chemistry*; John Wiley: Chichester, 1999; Chapter 9, p 219.



**Figure 1.** Photomodulated voltammogram of  $C_6H_5S^\bullet$  generated by photolysis of 10 mM diphenyl disulfide (eq 1) at a platinum electrode in a 0.1 M  $Bu_4NBF_4$ /acetonitrile solution. The voltammogram has been corrected for a slight drift in the background current. The sweep rate is  $0.1 \text{ V s}^{-1}$ .

disulfide (eq 1), with the two characteristic steady-state waves pertaining to the generalized electrode processes depicted in eqs 5 and 6. It was quite encouraging to find that the alternative



methods of generating  $C_6H_5S^\bullet$  through the hydrogen abstraction route involving  $C_6H_5SH$  (eqs 2 and 3) or by photolysis of  $C_6H_5SCl$  (eq 4) led to exactly the same voltammetric behavior, thus confirming the identity of the radical studied.

In Table 1 the half-wave potentials,  $E_{1/2}^{ox}$  and  $E_{1/2}^{red}$ , obtained for the series of para-substituted phenylthiyl radicals at a gold minigrad electrode are collected along with  $|E_{3/4} - E_{1/4}|$  values, which provide a measure of the width of the waves, as well as standard potentials  $E_{XC_6H_4S^\bullet}^\circ$ , available in the literature for some of the radicals.<sup>36</sup> Before discussing the trend in the values of  $E_{1/2}^{ox}$  and  $E_{1/2}^{red}$ , we need to consider in greater detail their thermodynamic significance. Voltammetric waves as shown in Figure 1 may be affected not only by fast homogeneous reactions involving  $XC_6H_4S^-$ ,  $XC_6H_4S^\bullet$ , or  $XC_6H_4S^+$  but also by slow charge-transfer kinetics associated with the electrode processes depicted in eqs 5 and 6. In particular, the latter factor could be rather crucial and shift the values of  $E_{1/2}^{ox}$  and  $E_{1/2}^{red}$  substantially by several hundred millivolts in positive and negative directions, respectively, compared with the thermodynamically significant  $E^\circ$  values. However, for most of the aromatic sulfur compounds selected in this paper, it does not seem to present a serious problem as witnessed by previous determinations of rather large values of the standard heterogeneous rate constants in the order of  $0.1 \text{ cm s}^{-1}$  for the oxidation of substituted thiophenoxides at a gold electrode in linear sweep voltammetry.<sup>36</sup> This is also consistent with the quite sharp rise observed in the oxidation and reduction waves in Figure 1 for the phenylthiyl radical with  $|E_{3/4} - E_{1/4}| = 80$  and  $65 \text{ mV}$ , respectively, which is not so far from the  $56.4 \text{ mV}$  expected for a Nernstian process.<sup>37</sup> For the oxidation waves pertaining to  $X = NH_2$  and  $OCH_3$ , the  $|E_{3/4} - E_{1/4}|$  values of  $126$  and  $140 \text{ mV}$  are somewhat larger, pointing toward the presence of a

greater quasi-reversible nature of the charge-transfer processes in these cases.

As to the homogeneous processes, dimerization of  $XC_6H_4S^\bullet$  or nucleophilic attack on  $XC_6H_4S^+$  by the solvent acetonitrile, the parent disulfide compound, residual water, or other nucleophilic impurities present in the solution does without doubt take place. For instance, the reaction of  $XC_6H_4S^+$  with acetonitrile would lead to the formation of the nitrilium ion  $XC_6H_4SN^+CCH_3$ .<sup>11</sup> In contrast to this behavior stands the high stability of  $XC_6H_4S^-$  in deaerated acetonitrile. It was noted that variation of the disulfide concentration or even addition of  $100 \text{ mM}$  nucleophiles such as tetrabutylammonium acetate or cyclohexene had almost no effect on the oxidation wave, shifting it in negative direction by no more than  $20 \text{ mV}$ . This indicates that the influence of follow-up reactions involving  $XC_6H_4S^+$  is small, presumably because the kinetic control is mainly by the quasi-reversible charge-transfer process at the electrode.

Some of the experiments in this study were also carried out at a platinum minigrad electrode or a carbon fiber net in order to elucidate the possible influence of adsorption phenomena. Interestingly, the measurements were found to be independent of whether platinum or gold was employed as electrode material, indicating that adsorption of the sulfur species at these electrode surfaces should present no serious problems. In the previous study concerning the use of fast cyclic voltammetry on substituted thiophenoxides at a gold electrode, it was even possible to attain reversibility for 4-methoxythiophenoxide and 4-methylthiophenoxide.<sup>36</sup> These observations are somewhat surprising, keeping the well-known ability of sulfur to form bonds to gold in mind. At carbon, on the other hand, the waves were broader and the quality of the curves was found to be quite dependent on the substituent. For instance, the results obtained for the phenylthiyl radical at carbon ( $E_{1/2}^{ox} = 0.79$  and  $E_{1/2}^{red} = 0.14 \text{ V vs SCE}$ ) almost did not differ from those obtained at gold ( $E_{1/2}^{ox} = 0.79$  and  $E_{1/2}^{red} = 0.16 \text{ V vs SCE}$ ) while the difference in the oxidation potentials obtained for the 4-methoxyphenylthiyl radical at carbon and gold amounted to as much as  $0.16 \text{ V}$  ( $E_{1/2}^{ox} = 0.84$  and  $0.68 \text{ V vs SCE}$  at carbon and gold, respectively). For this reason, we decided not to employ the carbon net any further in the present study.

To conclude on the above analysis of the quality of the experimental data, the values of  $E_{1/2}^{ox}$  and  $E_{1/2}^{red}$  cannot a priori be set equal to the standard potentials  $E_{XC_6H_4S^+}^\circ$  and  $E_{XC_6H_4S^\bullet}^\circ$ , as the systems under investigation are not strictly reversible. The difference between  $E_{1/2}$  and  $E^\circ$  is difficult to estimate quantitatively from an analysis of the voltammetric curves due to the combined effect of homogeneous and heterogeneous kinetics, and this is so not just for photomodulated voltammetry but for almost any other electrochemical technique.<sup>38</sup> However, in the case of photomodulated voltammetry, things are further complicated by the fact that the distribution of the photolytically generated radicals in the electrochemical cell will be non-homogeneous caused by the variable light intensity along the absorption path and, in particular, the shielding effect of the minigrad electrode.<sup>39</sup> Fortunately, the thermodynamic significance of five of the measured  $E_{1/2}^{red}$  values can be checked through a comparison with  $E_{XC_6H_4S^\bullet}^\circ$  values obtained previously in fast cyclic voltammetry.<sup>36</sup> As seen in Table 1, agreement between the two sets of  $E_{1/2}^{red}$  and  $E_{XC_6H_4S^\bullet}^\circ$  data is observed with a standard deviation of only  $40 \text{ mV}$  in the differences. This is so even if the width of the photomodulated voltammograms in

(36) Andrieux, C. P.; Hapiot, P.; Pinson, J.; Savéant, J.-M. *J. Am. Chem. Soc.* **1993**, *115*, 7783.

(37) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; John Wiley: New York, 1980.

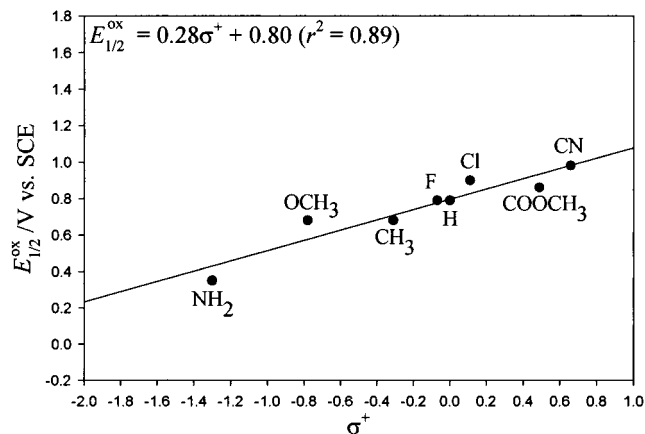
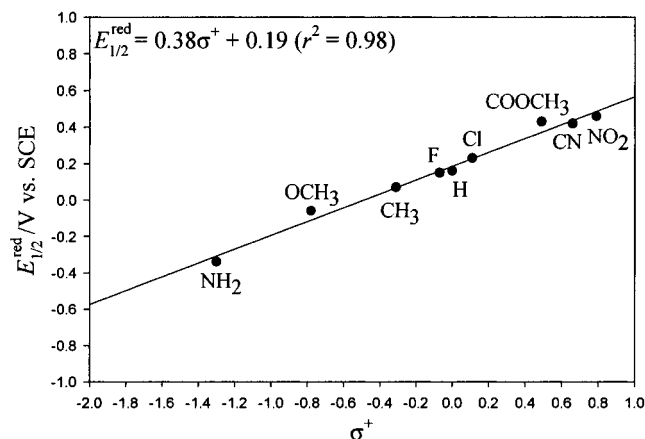
(38) Nagaoka, T.; Griller, D.; Wayner, D. D. M. *J. Phys. Chem.* **1991**, *95*, 6264.

(39) Birk, J. R.; Perone, S. P. *Anal. Chem.* **1968**, *40*, 496.

**Table 1.** Half-Wave Potentials,  $E_{1/2}^{\text{ox}}$  and  $E_{1/2}^{\text{red}}$ , Measured for  $\text{XC}_6\text{H}_4\text{S}^{\bullet}$  by Means of Photomodulated Voltammetry in 0.1 M  $\text{Bu}_4\text{NBF}_4$ /Acetonitrile at 24–26 °C at a Gold Minigrad Electrode unless Otherwise Noted<sup>a</sup>

X	method <sup>b</sup>	$E_{1/2}^{\text{ox}}$ <sup>c</sup>	$ E_{3/4} - E_{1/4} ^d$	$E_{1/2}^{\text{red}}$ <sup>c</sup>	$ E_{3/4} - E_{1/4} ^d$	$E_{\text{XC}_6\text{H}_4\text{S}^{\bullet}}^{\circ}$ <sup>c,e</sup>
NH <sub>2</sub>	1	0.35 <sup>f</sup>	126	-0.34	100	
OCH <sub>3</sub>	1, 2	0.68	140	-0.06	115	-0.035
CH <sub>3</sub>	1	0.68	57	0.07	84	0.040
F	1	0.79 <sup>f</sup>	94	0.15 <sup>f</sup>	93	
H	1, 2, 3	0.79 <sup>f</sup>	80	0.16 <sup>f</sup>	65	0.100
Cl	1, 2	0.90	93	0.23	99	0.180
COOCH <sub>3</sub>	1	0.86	80	0.43	99	
CN	1	0.98	84	0.42	88	
NO <sub>2</sub>	1, 2	g	g	0.46	68	0.455

<sup>a</sup> The uncertainty is  $\pm 40$  mV, average of at least four determinations. <sup>b</sup> Method 1, see eq 1; method 2, see eqs 2 and 3; method 3, see eq 4. <sup>c</sup> V vs SCE. <sup>d</sup> In mV. <sup>e</sup> From ref 36, measured at a gold ultramicroelectrode in acetonitrile. <sup>f</sup> These potentials were reproducible within 40 mV when measured at a platinum minigrad electrode. <sup>g</sup> No reproducible oxidation wave was observable in this case.

**Figure 2.** Plot of  $E_{1/2}^{\text{ox}}$  against the Hammett substituent coefficient  $\sigma^+$ .**Figure 3.** Plot of  $E_{1/2}^{\text{red}}$  against the Hammett substituent coefficient  $\sigma^+$ .

question shows a quite large variation with  $|E_{3/4} - E_{1/4}|$  going from 65 mV for  $\text{X} = \text{H}$  to 115 mV for  $\text{X} = \text{OCH}_3$ . On this basis and the fact that all other photomodulated waves show similar characteristics with  $|E_{3/4} - E_{1/4}|$  ranging from 57 to 140 mV, we assume that the measured  $E_{1/2}^{\text{ox}}$  and  $E_{1/2}^{\text{red}}$  values listed in Table 1 all are within 40 mV of the pertinent  $E_{\text{XC}_6\text{H}_4\text{S}^{\bullet}}^{\circ}$  and  $E_{\text{XC}_6\text{H}_4\text{S}^{\bullet}}^{\circ}$  values.

In Figures 2 and 3, the values of  $E_{1/2}^{\text{ox}}$  and  $E_{1/2}^{\text{red}}$  are plotted against the Hammett substituent coefficient  $\sigma^+$ . The slopes of 0.28 and 0.38 V/unit listed in the figures correspond to  $\rho^+$  values of 4.7 and 6.4, respectively. The  $\sigma^+$  parameter was used rather than  $\sigma$  or  $\sigma^-$  in order to be consistent with previous correlations reported for the reduction potentials of substituted phenylthiyl radicals in aprotic solvents<sup>36,40,41</sup> and water<sup>42</sup> and phenoxy radicals in acetonitrile<sup>43</sup> and water.<sup>44</sup> Actually, the values of  $E_{1/2}^{\text{red}}$  (but not  $E_{1/2}^{\text{ox}}$ ) were found to be almost equally well

**Table 2.** Hammett Slopes  $\rho^+$  Obtained for the Reduction and Oxidation Potentials of Substituted Phenylthiyl and Phenoxy Radicals in Different Solvents<sup>a</sup>

redox couple	$\rho^+$	solvent	lit.
$\text{RS}^{\bullet}/\text{RS}^{-\bullet}$ <sup>b</sup>	6.6	sulfolane/3-methylsulfolane (5%)	40
$\text{RS}^{\bullet}/\text{RS}^{-\bullet}$ <sup>b</sup>	6.7	dimethyl sulfoxide	41
$\text{RS}^{\bullet}/\text{RS}^{-\bullet}$ <sup>c</sup>	5.4	acetonitrile	36
$\text{RS}^{\bullet}/\text{RS}^{-\bullet}$ <sup>c</sup>	6.4	acetonitrile	this study
$\text{RS}^{\bullet}/\text{RS}^{-\bullet}$ <sup>d</sup>	3.7	water	42
$\text{RO}^{\bullet}/\text{RO}^{-\bullet}$ <sup>c</sup>	10.1	acetonitrile	43
$\text{RO}^{\bullet}/\text{RO}^{-\bullet}$ <sup>d</sup>	7.0	water	44
$\text{RS}^{\bullet}/\text{RS}^{\bullet}$	4.7	acetonitrile	this study

<sup>a</sup> In all cases, the potentials were correlated to the Hammett substituent coefficient  $\sigma^+$ . <sup>b</sup> Irreversible oxidation potentials of the thiophenoxides measured in linear sweep voltammetry. <sup>c</sup> Standard potentials obtained by means of fast cyclic voltammetry. <sup>d</sup> Standard potentials obtained by means of pulse radiolysis.

correlated with  $\sigma$  where the following relationship ensued:  $E_{1/2}^{\text{red}} = 0.55\sigma + 0.10$  ( $r^2 = 0.95$ ). The plot of  $E_{1/2}^{\text{red}}$  against  $\sigma^-$  was scattered due to a substantial deviation of the point pertaining to  $\text{NH}_2$ .

In Table 2 we have collected all relevant correlations obtained in this and previous studies for substituted phenylthiyl and phenoxy radicals. The fact that the values of  $\rho^+$  are positive for both the oxidation and reduction processes is in agreement with the expectation that the presence of electron-donating para substituents should make it harder to reduce both the phenylsulfenium cations and phenylthiyl radicals because of the stabilizing and destabilizing effects of such substituents on the cations and anions, respectively. The reason for the  $\rho^+$  value being smaller for phenylthiyl than phenoxy radicals is that the interaction with the  $\pi$  aromatic system is much less in the former kind of systems as noted by Armstrong et al.<sup>42</sup> Another feature of the results is that the slopes are smaller for aqueous solution than acetonitrile. This phenomenon can be attributed to the ability of water to stabilize anions (and in particular localized anions) through hydrogen bonding. Thus, the effect of the substituent on the electrode potentials is diminished due to solvation; i.e., the reduction of the difficult reducible phenylthiyl and phenoxy radicals having electron-donating para substituents proceeds relatively easier when the solvent is water rather than acetonitrile.

(40) Venimadhavan, S.; Amarnath, K.; Harvey, N. G.; Cheng, J.-P.; Arnett, E. M. *J. Am. Chem. Soc.* **1992**, *114*, 221.

(41) Bordwell, F. G.; Zhang, X.-M.; Satish, A. V.; Cheng, J.-P. *J. Am. Chem. Soc.* **1994**, *116*, 6605.

(42) Armstrong, D. A.; Sun, Q.; Schuler, R. H. *J. Phys. Chem.* **1996**, *100*, 9892.

(43) Hapiot, P.; Pinson, J.; Yousfi, N. *New J. Chem.* **1992**, *16*, 877.

(44) Lind, J.; Shen, X.; Eriksen, T. E.; Merényi, G. *J. Am. Chem. Soc.* **1990**, *112*, 479.

**Table 3.** Ionization Potentials, IP, Electron Affinities, EA, Differences in Solvation Energies,  $\Delta\Delta G_{\text{sol}}^{\circ}(+)$ ,  $\Delta\Delta G_{\text{sol}}^{\circ}(-)$ , and  $\Delta\Delta G_{\text{sol}}^{\circ}(\pm)$ , and Mulliken Charges on the Sulfur Atom in  $\text{XC}_6\text{H}_4\text{S}^+$  and  $\text{XC}_6\text{H}_4\text{S}^-$ <sup>a</sup>

X	IP <sup>b</sup>	EA <sup>b</sup>	$-\Delta\Delta G_{\text{sol}}^{\circ}(+)^c$	$-\Delta\Delta G_{\text{sol}}^{\circ}(-)^c$	$\Delta\Delta G_{\text{sol}}^{\circ}(\pm)^c$	charge on sulfur	
						cation	anion
NH <sub>2</sub>	7.16	1.87	48	58	11	+0.16	-0.67
OCH <sub>3</sub>	7.55	2.05	49	61	12	+0.19	-0.64
CH <sub>3</sub>	7.56	2.65	49	50	0	+0.24	-0.65
F	7.90	2.85	55	47	-8	+0.27	-0.66
H	7.98	2.70	56 <sup>d</sup>	51 <sup>d</sup>	-6 <sup>d</sup>	+0.29	-0.66
Cl	7.85	2.96	51	46	-5	+0.26	-0.63
COOCH <sub>3</sub>	8.48	2.79	66	55	-12	+0.27	-0.56
CN	8.18	3.24	57	44	-12	+0.27	-0.58
NO <sub>2</sub>	8.84	3.60		37		+0.33	-0.51

<sup>a</sup> For a discussion of the uncertainties involved in these calculations, see text. <sup>b</sup> In eV, calculated at the B3LYP/6-31++G\*\* level. <sup>c</sup> In kcal mol<sup>-1</sup>. <sup>d</sup> If the experimental values of IP = 8.63 eV and EA = 2.26 eV are used,<sup>7</sup> the following solvation energies are obtained:  $-\Delta\Delta G_{\text{sol}}^{\circ}(+) = 71$  kcal mol<sup>-1</sup>,  $-\Delta\Delta G_{\text{sol}}^{\circ}(-) = 61$  kcal mol<sup>-1</sup>, and  $\Delta\Delta G_{\text{sol}}^{\circ}(\pm) = -11$  kcal mol<sup>-1</sup>.

**Solvation Energies.** The slopes of the Hammett plots are larger for the reduction ( $\rho^+ = 6.4$ ) than oxidation processes ( $\rho^+ = 4.7$ ), indicating that the substituent effect is larger on  $E_{1/2}^{\text{red}}$  than  $E_{1/2}^{\text{ox}}$ . To have a better understanding of such a result and in general of the thermochemistry of sulfur-centered species, we turned our attention toward a calculation of the ionization potential, IP, and the electron affinity, EA, of  $\text{XC}_6\text{H}_4\text{S}^{\bullet}$  and on this basis the solvation energies of the corresponding ions,  $\Delta G_{\text{sol}}^{\circ}(\text{XC}_6\text{H}_4\text{S}^+)$  and  $\Delta G_{\text{sol}}^{\circ}(\text{XC}_6\text{H}_4\text{S}^-)$ . The formal relationships used for extracting the latter two parameters from thermochemical cycles have long been recognized (eqs 7–9).<sup>45,46</sup>

$$\Delta\Delta G_{\text{sol}}^{\circ}(+) \equiv \Delta G_{\text{sol}}^{\circ}(\text{XC}_6\text{H}_4\text{S}^+) - \Delta G_{\text{sol}}^{\circ}(\text{XC}_6\text{H}_4\text{S}^{\bullet}) = -\text{IP} + FE_{\text{XC}_6\text{H}_4\text{S}^+}^{\circ} + C \quad (7)$$

$$\Delta\Delta G_{\text{sol}}^{\circ}(-) \equiv \Delta G_{\text{sol}}^{\circ}(\text{XC}_6\text{H}_4\text{S}^-) - \Delta G_{\text{sol}}^{\circ}(\text{XC}_6\text{H}_4\text{S}^{\bullet}) = \text{EA} - FE_{\text{XC}_6\text{H}_4\text{S}^-}^{\circ} - C \quad (8)$$

$$\Delta\Delta G_{\text{sol}}^{\circ}(\pm) \equiv \Delta G_{\text{sol}}^{\circ}(\text{XC}_6\text{H}_4\text{S}^+) - \Delta G_{\text{sol}}^{\circ}(\text{XC}_6\text{H}_4\text{S}^-) = -(\text{IP} + \text{EA}) + F(E_{\text{XC}_6\text{H}_4\text{S}^-}^{\circ} + E_{\text{XC}_6\text{H}_4\text{S}^+}^{\circ}) + 2C \quad (9)$$

Strictly speaking, the use of IP and EA in these equations is based on the approximation that they are equal to the corresponding Gibbs energy entities. The parameter  $\Delta G_{\text{sol}}^{\circ}(\text{XC}_6\text{H}_4\text{S}^{\bullet})$  is the solvation energy of  $\text{XC}_6\text{H}_4\text{S}^{\bullet}$  and  $C$  is a constant that depends on the reference electrode. In this paper, a number of 109.3 kcal mol<sup>-1</sup> is used for  $C$ , which originates from the absolute potential of the standard calomel electrode ( $= -4.74$  V) determined as an average of five separate measurements.<sup>47,48</sup> The standard potentials  $E_{\text{XC}_6\text{H}_4\text{S}^+}^{\circ}$  and  $E_{\text{XC}_6\text{H}_4\text{S}^-}^{\circ}$  were approximated by the half-wave potentials  $E_{1/2}^{\text{ox}}$  and  $E_{1/2}^{\text{red}}$ , respectively, with the notion that these sets of potentials are within 40 mV of each other. The adiabatic IP and EA values were obtained by means of density functional theory calculations. For  $\text{C}_6\text{H}_5\text{S}^{\bullet}$ , the deviation of the calculated IP and EA values (7.98 and 2.70 eV, respectively) from the experimentally known values<sup>7</sup> of 8.63 and 2.26 eV constitutes 10–20%, which ultimately leads to an underestimation of  $-\Delta\Delta G_{\text{sol}}^{\circ}(+)$  and  $-\Delta\Delta G_{\text{sol}}^{\circ}(-)$  by as much as 15 and 10 kcal mol<sup>-1</sup>, respectively. Unfortunately, there are no experimental IP and EA data available for any of the substituted phenylthiyl radicals, preventing a more thorough test of the reliability of the calculations. Still, the calculations are expected to provide a consistent set

of relative results for the series of structurally similar compounds selected herein.

The dominant solvation terms in eqs 7 and 8 will be the ones of the ions rather than  $\Delta G_{\text{sol}}^{\circ}(\text{XC}_6\text{H}_4\text{S}^{\bullet})$  due to the solvation of a charge. This does not mean that the contribution from  $\Delta G_{\text{sol}}^{\circ}(\text{XC}_6\text{H}_4\text{S}^{\bullet})$  is negligible since the solubility of the organic radicals—some of them containing rather strong dipoles because of the substituent—must be appreciable in acetonitrile. In this sense, the most interesting results are perhaps not the  $\Delta\Delta G_{\text{sol}}^{\circ}(+)$  and  $\Delta\Delta G_{\text{sol}}^{\circ}(-)$  values but rather their difference as expressed in eq 9,  $\Delta\Delta G_{\text{sol}}^{\circ}(\pm)$ . Being independent of the radical species,  $\Delta\Delta G_{\text{sol}}^{\circ}(\pm)$  describes quite adequately the trend in the solvation features of the ions. At the same time, the uncertainty on the calculation of  $\Delta\Delta G_{\text{sol}}^{\circ}(\pm)$  is lower than the uncertainties on  $\Delta\Delta G_{\text{sol}}^{\circ}(+)$  and  $\Delta\Delta G_{\text{sol}}^{\circ}(-)$  since the deviations of the calculated EA and IP values from the corresponding experimental values seem to cancel when EA and IP are summed. At least this is the case for the phenylthiyl radical, where the difference in the  $\Delta\Delta G_{\text{sol}}^{\circ}(\pm)$  values obtained on the basis of the calculated and experimental EA and IP data becomes as small as 5 kcal mol<sup>-1</sup> as compared to the 15 and 10 kcal mol<sup>-1</sup> found for  $\Delta\Delta G_{\text{sol}}^{\circ}(+)$  and  $\Delta\Delta G_{\text{sol}}^{\circ}(-)$ , respectively.

In Table 3, the solvation energies  $-\Delta\Delta G_{\text{sol}}^{\circ}(+)$ ,  $-\Delta\Delta G_{\text{sol}}^{\circ}(-)$ , and  $\Delta\Delta G_{\text{sol}}^{\circ}(\pm)$  are collected along with the IP and EA values and calculated Mulliken charges on sulfur. Note that the substituents are listed in order of their  $\sigma^+$  values. A plot of IP versus EA reveals a reasonable linear relationship with a slope of 0.82 ( $r^2 = 0.74$ ); i.e., the substituent effect is larger on EA than IP. From a comparison of this value with the slope of 0.72 ( $r^2 = 0.89$ ) found for a corresponding plot of  $E_{1/2}^{\text{ox}}$  vs  $E_{1/2}^{\text{red}}$ , it follows that the substituent dependency on the solvation energies of the series of phenylsulfonium cations and thiophenoxides cannot be too different.<sup>49</sup> A more detailed picture of these features is revealed from the calculated  $-\Delta\Delta G_{\text{sol}}^{\circ}(+)$  and  $-\Delta\Delta G_{\text{sol}}^{\circ}(-)$  values, although it should be kept in mind that these numbers also include a nonnegligible contribution from  $\Delta G_{\text{sol}}^{\circ}(\text{XC}_6\text{H}_4\text{S}^{\bullet})$  and that they presumably are somewhat underestimated due to the uncertainty present in the calculations of EA and IP.

The values of  $-\Delta\Delta G_{\text{sol}}^{\circ}(-)$  shown in column 5 vary from 37 to 61 kcal mol<sup>-1</sup> going from X = NO<sub>2</sub> to CH<sub>3</sub>O; i.e.,  $-\Delta\Delta G_{\text{sol}}^{\circ}(-)$  tends to decrease as the electron-withdrawing

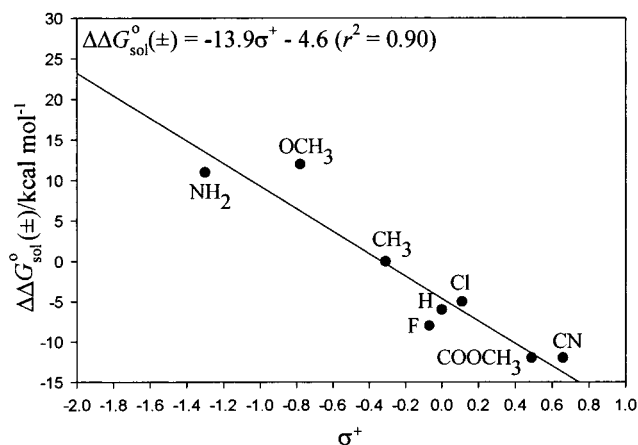
(49) In this context it might be mentioned that the slope of a plot of  $FE_{1/2}^{\text{red}}$  vs EA is 0.44, which is comparable to the value of 0.40 found for the slope in a plot of  $FE_{1/2}^{\text{ox}}$  vs IP. The reason both slopes are smaller than 1—the expected value according to eqs 7 and 8 if  $\Delta\Delta G_{\text{sol}}^{\circ}(-)$  and  $\Delta\Delta G_{\text{sol}}^{\circ}(+)$  were constant throughout the series—is due to the substituent effects on  $\Delta\Delta G_{\text{sol}}^{\circ}(-)$  and  $\Delta\Delta G_{\text{sol}}^{\circ}(+)$ .

(45) Matsen, F. A. *J. Chem. Phys.* **1956**, *24*, 602.

(46) Peover, M. E. *Trans. Faraday Soc.* **1962**, *58*, 1656.

(47) Reiss, H.; Heller, A. *J. Phys. Chem.* **1985**, *89*, 4207.

(48) Lim, C.; Bashford, D.; Karplus, M. *J. Phys. Chem.* **1991**, *95*, 5610.



**Figure 4.** Plot of  $\Delta\Delta G_{\text{sol}}^{\circ}(\pm)$  against the Hammett substituent coefficient  $\sigma^+$ .

ability of the substituent is enhanced. The substituent  $\text{COOCH}_3$  with its relatively large value of  $55 \text{ kcal mol}^{-1}$  represents a clear exception from this trend. Calculations of the Mulliken charge on the sulfur atom (column 8) reveal as expected that the most delocalized systems are the ones having electron-withdrawing groups pulling negative charge density from the sulfur atom into the  $\pi$  system. For instance, the Mulliken charge is  $-0.64$  for  $\text{X} = \text{CH}_3\text{O}$  whereas it is  $-0.51$  for  $\text{X} = \text{NO}_2$ . Hence, the general expectation of a decrease in  $-\Delta\Delta G_{\text{sol}}^{\circ}(-)$  as the charge becomes more delocalized is met,<sup>50–52</sup> even if specific exceptions, as the one mentioned above, may be found. Another exception pertains to the observation that the decrease in  $-\Delta\Delta G_{\text{sol}}^{\circ}(-)$  going from  $\text{X} = \text{NH}_2$  or  $\text{OCH}_3$  to  $\text{X} = \text{F}$  or  $\text{H}$  is not reflected in the finding of appreciably different Mulliken charges.

The values of  $-\Delta\Delta G_{\text{sol}}^{\circ}(+)$  listed in column 4 are in the range  $48\text{--}57 \text{ kcal mol}^{-1}$  for all substituents but  $\text{COOCH}_3$ , in the case of which a surprisingly large value of  $66 \text{ kcal mol}^{-1}$  is found. The variation in the solvation energy of the phenylsulfenium cations is thus relatively small, but it does exhibit a substituent dependency as was the case for  $-\Delta\Delta G_{\text{sol}}^{\circ}(-)$  with the important notion that the largest values of  $-\Delta\Delta G_{\text{sol}}^{\circ}(+)$  now are found for the electron-withdrawing groups. The explanation for this behavior again seems to reside in the charge distribution in the sulfenium cations as the Mulliken charge on sulfur ranges from  $+0.16$  to  $+0.33$  going from  $\text{X} = \text{NH}_2$  to  $\text{X} = \text{NO}_2$  (see column 7). Interestingly, the charge delocalization is found to be much more pronounced for the phenylsulfenium cations than for the thiophenoxides, meaning that sulfur should not be as important a solvation site for the cations. However, such an interpretation is contradicted by the general finding of large values of  $-\Delta\Delta G_{\text{sol}}^{\circ}(+)$  and therefore it will be discussed in greater detail in the following.

The values of  $\Delta\Delta G_{\text{sol}}^{\circ}(\pm)$  listed in column 6 are interesting from the point of view that they are independent of  $\Delta G_{\text{sol}}^{\circ}(\text{XC}_6\text{H}_4\text{S}^{\bullet})$  and better reveal the differences in the solvation behaviors of the two sets of ions. In Figure 4,  $\Delta\Delta G_{\text{sol}}^{\circ}(\pm)$  is plotted against  $\sigma^+$ , which provides a suitable measure of the substituent effect. At least a couple of points are worth noting. First, the overall trend in  $\Delta\Delta G_{\text{sol}}^{\circ}(\pm)$  shows a decrease as the electron-withdrawing ability of the substituent is enhanced, which indeed is expected from the observed substituent effects

on  $\Delta\Delta G_{\text{sol}}^{\circ}(+)$  and  $\Delta\Delta G_{\text{sol}}^{\circ}(-)$ . Second, the point pertaining to the substituent  $\text{COOCH}_3$  does not fall off the line as seen for the sets of  $\Delta\Delta G_{\text{sol}}^{\circ}(+)$  and  $\Delta\Delta G_{\text{sol}}^{\circ}(-)$  values. This indicates that the unusual solvation behavior in this specific case should not be attributed to the ions but rather to an exceptionally large value of  $\Delta G_{\text{sol}}^{\circ}(\text{XC}_6\text{H}_4\text{S}^{\bullet})$ . Third, the sign of the  $\Delta\Delta G_{\text{sol}}^{\circ}(\pm)$  values shows that acetonitrile is better in solvating phenylsulfenium cations than thiophenoxides unless strong electron-donating groups such as  $\text{OCH}_3$  and  $\text{NH}_2$  are considered. This is a somewhat surprising result as emphasized above since the charge localization on the sulfur atom in the thiophenoxides is pronounced with calculated Mulliken charges in the range of  $-0.67$  to  $-0.51$  as compared to the values of  $+0.16$  to  $+0.33$  found for the corresponding phenylsulfenium cations.

In this context, it is of interest to look at solvation data available for other ions such as the benzyl cation and anion, various aromatic radical cations and anions, and the isoelectronic and localized  $\text{K}^+$  and  $\text{Cl}^-$  ions. For the benzyl ions in acetonitrile:  $-\Delta\Delta G_{\text{sol}}^{\circ}(+) = 40 \text{ kcal mol}^{-1}$  and  $-\Delta\Delta G_{\text{sol}}^{\circ}(-) = 57 \text{ kcal mol}^{-1}$ ; i.e.,  $\Delta\Delta G_{\text{sol}}^{\circ}(\pm) = 17 \text{ kcal mol}^{-1}$ .<sup>28</sup> Calculation of the Mulliken populations in these two ions shows a large difference in the charge distribution; while the charge at the benzylic carbon is  $-0.70$  for the anion it is  $-0.18$  for the cation, which is a benign consequence of the polarization of the  $\text{CH}$  bonds toward carbon. With respect to our study on the sulfur-centered ions, these results are best comparable to the data obtained for  $\text{X} = \text{NH}_2$  or  $\text{OCH}_3$ , where  $\Delta\Delta G_{\text{sol}}^{\circ}(\pm) \approx 12 \text{ kcal mol}^{-1}$ .

The solvation study by Case et al.<sup>53</sup> of a series of alternant aromatic compounds such as anthracene, pyrene, and chrysene is interesting from the point of view that the charge distribution in the delocalized positive and negative ions of a given molecule is (largely) identical apart from the change of sign. It was found that the solvation energy of the cation was a few kilocalories per mole more negative than that of the anion, and this small difference was merely attributed to the surface potential of acetonitrile than a difference in the "chemical" solvation energy. For the localized and similar-sized  $\text{K}^+$  and  $\text{Cl}^-$  ions, the solvation energies are also similar as the following values are found by combining the known aqueous solvation energies with the relevant Gibbs free energies of transfer of the ions from water to acetonitrile:<sup>54</sup>  $-\Delta G_{\text{sol}}^{\circ}(\text{K}^+) = 71 \text{ kcal mol}^{-1}$  and  $-\Delta G_{\text{sol}}^{\circ}(\text{Cl}^-) = 73 \text{ kcal mol}^{-1}$ .

These literature results emphasize that there should be no reason for having a stronger solvation of cations than anions in acetonitrile unless there is a specific interaction between the cation and the solvent. Since it is well known that carbocations and presumably also sulfenium cations<sup>11</sup> react with acetonitrile in a Ritter reaction, it is possible that the specific solvation of the cation center by the nitrogen atom of acetonitrile is so strong that the positive charge is substantially more localized at this site than predicted by calculations. We therefore suspect that the calculated gas-phase Mulliken populations do not provide a completely adequate picture of the charge distribution in the solvated sulfenium cations.

## Conclusions

Oxidation and reduction potentials of a series of para-substituted phenylthiyl radicals  $\text{XC}_6\text{H}_4\text{S}^{\bullet}$  have been measured by means of photomodulated voltammetry in acetonitrile. Both sets of potentials correlate linearly with the Hammett substituent

(50) Wayner, D. D. M.; Sim, B. A.; Dannenberg, J. J. *J. Org. Chem.* **1991**, *56*, 4853.

(51) Daasbjerg, K. *Acta Chem. Scand.* **1995**, *49*, 878.

(52) Brinck, T.; Larsen, A. G.; Madsen, K. M.; Daasbjerg, K. *J. Phys. Chem. B* **2000**, *104*, 9887.

(53) Case, B.; Hush, N. S.; Parsons, R.; Peover, M. E. *J. Electroanal. Chem.* **1965**, *10*, 360.

(54) Marcus, Y. *Ion Solvation*; John Wiley: Chichester, 1985.

coefficient  $\sigma^+$ , giving slopes  $\rho^+$  of 4.7 and 6.4, respectively. This indicates that the substituent effect is larger on  $E_{1/2}^{\text{red}}$  than  $E_{1/2}^{\text{ox}}$ , which is a reflection of the development in the pertinent sets of EA and IP values of  $\text{XC}_6\text{H}_4\text{S}^*$ . Solvation energies extracted for  $\text{XC}_6\text{H}_4\text{S}^+$  and  $\text{XC}_6\text{H}_4\text{S}^-$  from thermochemical cycles show the expected substituent dependency for both kinds of ions; i.e., the absolute values of the solvation energies decrease as the charge becomes more delocalized. Acetonitrile is better in solvating  $\text{XC}_6\text{H}_4\text{S}^+$  than  $\text{XC}_6\text{H}_4\text{S}^-$  for most substituents even if quantum-mechanical calculations show a substantial charge delocalization in the series of phenylsulfenium cations. We suggest that this is due to a strong specific solvation

of the cation center by the nitrogen atom of acetonitrile and that the gas-phase calculations therefore do not provide a completely adequate picture of the charge distribution in the solvated ions. Finally, it should be noted that the substituent effect on  $E_{1/2}^{\text{red}}$  is smaller in aqueous solution than acetonitrile, which is attributed to the ability of water to stabilize in particular localized anions through hydrogen bonding.

**Acknowledgment.** We thank Statens Naturvidenskabelige Forskningsråd for financial support.

JA003811B