Redox Properties of 4-Substituted Aryl Methyl Chalcogenides in Water

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The one-electron reduction potentials of 14 4-substituted aryl methyl chalcogenide radical cations in water have been measured by pulse radiolysis. The reduction potentials were plotted against the Brown substituent constant of the 4-substituent giving straight lines with slopes close to zero. Aryl methyl chalcogenides with strongly electron-donating substituents deviated markedly from the general trend indicating a different nature of the radical cation. The results are compared with electrochemical results in organic solvents and with gas-phase ionization energies. This comparison shows that the substituent effect on the potential decreases with increasing polarity of the solvent. In addition, the redox properties of diaryl, dimethyl and aryl methyl sulfides are compared and discussed.

Organic tellurium compounds have been suggested to have antioxidant properties due to the rather low one-electron reduction potentials of the corresponding radical cations.[1,2] The recent finding that the reaction between oxidative peroxyl radicals and diaryl tellurides produces even more oxidative alkoxyl radicals strongly questions the suitability of these substances as antioxidants.[3] Nevertheless, the redox properties of organic tellurium compounds and other organic chalcogenides are of general chemical interest. The difference between diaryl, dialkyl and aryl alkyl chalcogenides deserves to be studied, as well as the remote substituent effects on the one-electron reduction potentials of 4,4′-substituted diaryl chalcogenides and 4-substituted aryl methyl chalcogenides. The redox nature of the latter is also interesting in relation to the general trend for 1,4-substituted benzene radical cations [eqn. (1)].[4]

$$E^\circ = 2.2 + 0.8\,(\sigma_{p1}^{+} + \sigma_{p4}^{+}) + 0.4\sigma_{p1}^{+}\sigma_{p4}^{+} \quad (\text{V } vs. \text{ NHE}) \qquad (1)$$

This also leads to the question of whether the charge on diaryl, dialkyl and aryl alkyl radical cations is localized on the chalcogen or whether it is delocalized. Were the latter case to apply, the substituent dependence should follow the empirically derived equation above; otherwise the effects of remote substituents should be weaker than expected from eqn. (1).

One-electron reduction potentials can be determined by electrochemical methods or by pulse radiolysis. The latter gives the equilibrium constant for the reversible reaction between two redox pairs and thus the thermodynamically correct reduction potential can be calculated [reaction (2)]. Since electrochemical methods are irreversible they can only give estimates or trends of the reduction potential.

$$(\text{4-R-Ph-X-Me})^{\bullet +} + \text{Ref.} \rightleftharpoons \text{4-R-Ph-X-Me} + \text{Ref.}^{\bullet +} \qquad (2)$$

The redox properties of diaryl chalcogenides and aryl methyl chalcogenides have been studied extensively in organic solvents by electrochemical methods.[1] Recently, the redox properties of diaryl chalcogenides in water were also subjected to pulse radiolytic studies.[5] In this work we have investigated the redox properties of 4-substituted aryl methyl chalcogenides (X = S, Se and Te) in water by pulse radiolysis.

Experimental

All aryl methyl chalcogenides except thioanisole were synthesized as described in the literature[1] by Dr. L. Engman. The other chemicals were of the purest grade available (Aldrich and Merck) and were used as supplied. Millipore Milli-Q filtered water was used throughout.

Radiolysis of water results in the formation of $^{\bullet}$OH, e_{aq}^-, H_2O_2, H_2 and H_3O^+, with $^{\bullet}$OH and e_{aq}^- being the major radical species with primary radiation chemical yields of 0.28 µmol J^{-1} each[6] above pH 3. Unless otherwise stated, N_2O-saturated solutions were used in order to convert the reducing solvated electron into the oxidizing hydroxyl radical[6] (G_{OH} = 0.56 µmol J^{-1}).

The pulse radiolysis equipment consists of a linear accelerator delivering 3 MeV electrons and a computerized optical detection system.[7] The pulses were of 5–10 ns duration giving doses of 3–6 Gy. For dosimetry a N_2O-saturated 10^{-2} mol dm^{-3} KSCN solution was used.[8] The $G\varepsilon$ value of $(SCN)_2^{\bullet -}$ was taken to be 4.78×10^{-4} m^2 J^{-1} at 500 nm.

Primary oxidation of the aryl methyl chalcogenides was carried out by $Br_2^{\bullet -}$ when measuring the spectral properties of the radical cations. $N_3^{\bullet}$ and $SO_4^{\bullet -}$ were used as primary oxidants when measuring the one-electron reduction potentials of the radical cations. These three primary oxidants were produced in the following way upon irradiation.

$$^{\bullet}OH + Br^- \longrightarrow OH^- + Br^{\bullet} \qquad (3a)$$

$$Br^{\bullet} + Br^- \longrightarrow Br_2^{\bullet -} \qquad (3b)$$

$$^{\bullet}OH + N_3^- \longrightarrow OH^- + N_3^{\bullet} \qquad (4)$$

$$e_{aq}^- + S_2O_8^{2-} \longrightarrow SO_4^{\bullet -} + SO_4^{2-} \qquad (5)$$

The above reactions have the following rate constants: $k_{3a} = 1.1 \times 10^{10}$ dm^3 mol^{-1} s^{-1},[9] $k_{3b} = 1.2 \times 10^{10}$ dm^3 mol^{-1} s^{-1},[10] $k_4 = 1.2 \times 10^{10}$ dm^3 mol^{-1} s^{-1} [9] and $k_5 = 1.1 \times 10^{10}$ dm^3 mol^{-1} s^{-1}.[9] The concentrations of Br^-, N_3^- and $S_2O_8^{2-}$ were 0.1, 10^{-2} and 10^{-2} mol dm^{-3}, respectively. When using $SO_4^{\bullet -}$ as primary oxidant, 2×10^{-2} mol dm^{-3} 2-methylpropan-2-ol was added to the Ar-purged solution in order to scavenge the hydroxyl radicals. Reduction potential measurements were performed at pH 7 (phosphate buffer).

Methods.—The one-electron reduction potentials of the 4-substituted aryl methyl chalcogenide radical cations were determined by measuring the equilibrium concentrations of radical cations or the radicals formed upon oxidation of the reference substance, with varying concentrations of 4-substituted aryl methyl chalcogenide and reference substance

Table 1 Experimental conditions for reduction potential measurements

Aryl methyl chalcogenide	Primary oxidant	Ref. substance	λ/nm
$4\text{-}(CH_3)_2N\text{–}C_6H_4\text{–}S\text{–}CH_3$	$N_3^{\bullet}$	$ABTS^{2-}$	430
$4\text{-}CH_3O\text{–}C_6H_4\text{–}S\text{–}CH_3$	$SO_4^{\bullet-}$	$1,2\text{-}(CH_3O)_2\text{–}C_6H_4$	580
$4\text{-}CH_3\text{–}C_6H_4\text{–}S\text{–}CH_3$	$SO_4^{\bullet-}$	$1,2\text{-}(CH_3O)_2\text{–}C_6H_4$	560
$C_6H_5\text{–}S\text{–}CH_3$	$SO_4^{\bullet-}$	$1,2\text{-}(CH_3O)_2\text{–}C_6H_4$	550
$4\text{-}CF_3\text{–}C_6H_4\text{–}S\text{–}CH_3$	$SO_4^{\bullet-}$	$4\text{-}CH_3O\text{–}C_6H_4\text{–}S\text{–}CH_3$	580
$4\text{-}(CH_3)_2N\text{–}C_6H_4\text{–}Se\text{–}CH_3$	$N_3^{\bullet}$	$ABTS^{2-}$	430
$4\text{-}CH_3O\text{–}C_6H_4\text{–}Se\text{–}CH_3$	$N_3^{\bullet}$	$4\text{-}I\text{–}C_6H_4\text{–}NH_2$	680
$4\text{-}CH_3\text{–}C_6H_4\text{–}Se\text{–}CH_3$	$N_3^{\bullet}$	$4\text{-}I\text{–}C_6H_4\text{–}NH_2$	560
$C_6H_5\text{–}Se\text{–}CH_3$	$N_3^{\bullet}$	$4\text{-}I\text{–}C_6H_4\text{–}NH_2$	560
$4\text{-}CF_3\text{–}C_6H_4\text{–}Se\text{–}CH_3$	$SO_4^{\bullet-}$	$1,2,4\text{-}(CH_3O)_3\text{–}C_6H_3$	460
$4\text{-}CH_3O\text{–}C_6H_4\text{–}Te\text{–}CH_3$	$N_3^{\bullet}$	$ABTS^{2-}$	430
$4\text{-}CH_3\text{–}C_6H_4\text{–}Te\text{–}CH_3$	$N_3^{\bullet}$	$ABTS^{2-}$	430
$C_6H_5\text{–}Te\text{–}CH_3$	$N_3^{\bullet}$	$ABTS^{2-}$	430
$4\text{-}CF_3\text{–}C_6H_4\text{–}Te\text{–}CH_3$	$N_3^{\bullet}$	$ABTS^{2-}$	430

Table 2 Rate constants, equilibrium constants and one-electron reduction potentials[a]

Radical cation	$k_f/10^9$ dm^3 mol^{-1} s^{-1}	k_r/dm^3 mol^{-1} s^{-1}	K_{kin}	K_{abs}	E° (V *vs.* NHE)
$[4\text{-}(CH_3)_2N\text{–}C_6H_4\text{–}S\text{–}CH_3]^{\bullet+}$	1.1 ± 0.4	(1.7 ± 0.2) × 10^9	0.6 ± 0.2	0.37 ± 0.05	0.65 ± 0.01
$[4\text{-}CH_3O\text{–}C_6H_4\text{–}S\text{–}CH_3]^{\bullet+}$	0.7 ± 0.3	(1.8 ± 0.2) × 10^9	0.4 ± 0.2	0.6 ± 0.1	1.43 ± <0.01
$[4\text{-}CH_3\text{–}C_6H_4\text{–}S\text{–}CH_3]^{\bullet+}$	0.2 ± 0.2	(2.5 ± 0.1) × 10^9	0.08 ± 0.08	0.4 ± 0.1	1.42 ± 0.02
$(C_6H_5\text{–}S\text{–}CH_3)^{\bullet+}$				1.8 ± 0.5	1.45 ± <0.01
$(4\text{-}CF_3\text{–}C_6H_4\text{–}S\text{–}CH_3)^{\bullet+}$	1.0 ± 0.1	(2 ± 1) × 10^8	5 ± 2	1.5 ± 0.2	1.45 ± 0.03
$[4\text{-}(CH_3)_2N\text{–}C_6H_4\text{–}Se\text{–}CH_3]^{\bullet+}$				0.47 ± 0.05	0.60 ± <0.01
$(4\text{-}CH_3O\text{–}C_6H_4\text{–}Se\text{–}CH_3)^{\bullet+}$	4.1 ± 0.7	(3 ± 1) × 10^8	14 ± 5	15 ± 2	1.09 ± <0.01
$(4\text{-}CH_3\text{–}C_6H_4\text{–}Se\text{–}CH_3)^{\bullet+}$	1.1 ± 0.1	(2.7 ± 0.9) × 10^9	4 ± 1	7.8 ± 0.3	1.07 ± 0.01
$(C_6H_5\text{–}Se\text{–}CH_3)^{\bullet+}$	6.8 ± 0.9	(1.8 ± 0.1) × 10^9	3.7 ± 0.6	7 ± 1	1.09 ± 0.01
$(4\text{-}CF_3\text{–}C_6H_4\text{–}Se\text{–}CH_3)^{\bullet+}$	4 ± 4	(5.7 ± 0.6) × 10^9	0.7 ± 0.7	10.5 ± 0.5	1.20 ± 0.02
$(4\text{-}CH_3O\text{–}C_6H_4\text{–}Te\text{–}CH_3)^{\bullet+}$	5.7 ± 0.8	(8 ± 1) × 10^8	7 ± 1	5.7 ± 0.5	0.73 ± <0.01
$(4\text{-}CH_3\text{–}C_6H_4\text{–}Te\text{–}CH_3)^{\bullet+}$	6.2 ± 0.7	(1.0 ± 0.2) × 10^9	6 ± 1	4.1 ± 0.5	0.72 ± <0.01
$(C_6H_5\text{–}Te\text{–}CH_3)^{\bullet+}$	3.8 ± 0.7	(1.3 ± 0.1) × 10^9	2.9 ± 0.6	10 ± 1	0.74 ± 0.01
$(4\text{-}CF_3\text{–}C_6H_4\text{–}Te\text{–}CH_3)^{\bullet+}$	6 ± 1	(8 ± 1) × 10^8	8 ± 2	11 ± 1	0.75 ± <0.01

[a] The one-electron reduction potentials are calculated from K_{abs}, since the uncertainty in K_{kin} is much greater in general. When the difference between K_{abs} and K_{kin} is greater than the uncertainty in K_{abs}, this difference is taken as the uncertainty. The uncertainties in the values of the reference substances have not been taken into account.

[reaction (2)].[11,12] The resulting equilibrium concentrations yield the equilibrium constant which can be inserted into the Nernst equation to calculate the one-electron reduction potential. The rates of equilibration can also be measured and used to obtain a kinetically determined equilibrium constant.

Equilibrium constants are preferably determined by plotting $1/A$ (A = absorbance at equilibrium) or k_{obs} against the ratio between the concentrations of 4-substituted aryl methyl chalcogenide and reference substance. The equilibrium constant is obtained from eqn. (6) which can be shown to hold for the

$$1/A = \left\{1 + \frac{[\text{Reference substance}]}{K[\text{Aryl methyl chalcogenide}]}\right\}\frac{1}{A^\circ} \qquad (6)$$

equilibrium [reaction (2)]. A° is the maximum signal obtainable. The forward and reverse rate constants used to calculate the 'kinetic' equilibrium constant were determined using relationship (7).

$$k_{obs} = k_f[\text{Aryl methyl chalcogenide}] + k_r[\text{Reference substance}] \qquad (7)$$

In Table 1 the experimental conditions for reduction potential measurements are given. The reference substances (reduced form given) employed were $1,2\text{-}(CH_3O)_2\text{–}C_6H_4$, $1,2,4\text{-}(CH_3O)_3\text{–}C_6H_3$, $4\text{-}I\text{–}C_6H_4\text{–}NH_2$, $ABTS^{2-}$ [2,2′-azinobis(3-ethylbenzothiazole-6-sulfonate)] and promethazine [10-(2-dimethylaminopropyl)phenothiazine], their one-electron reduction potentials *vs.* NHE being 1.44 V,[4] 1.13 V,[4] 1.02 V,[13] 0.68 V[14] and 0.91 V,[13] respectively.

Results and Discussion

Spectral Properties.—In Fig. 1(*a*)–(*c*) the differential spectra between the aryl methyl chalcogenide radical cations and the corresponding aryl methyl chalcogenides are given. The general trend is that the more electron donating the 4-substituent, the higher is the wavelength of maximum absorption. Thus, delocalization of charge increases with electron donating ability of the substituent. The extinction coefficients also increase going from electron-withdrawing to electron-donating substituents.

One-electron Reduction Potentials.—Table 2 compiles the redox rate constants, k_f and k_r, equilibrium constants, K_{abs} and K_{kin} (derived using the two methods previously described) and the one-electron reduction potentials, E° [(4-R–Ph–X–Me)$^{\bullet+}$/4-R–Ph–X–Me]. The approximate first half-life of the radical cations in the absence of a reference substance is 5–10 × 10^{-5} s and the approximate half-lives for redox equilibration in the presence of a reference substance is 1 × 10^{-6} s. Thus the radical cations are sufficiently stable for redox measurements.

To elucidate the substituent effects on the one-electron reduction potentials of 4-substituted aryl methyl chalcogenide radical cations we have plotted the reduction potentials against the Brown substituent constants, σ_p^+ (Fig. 2).[15]

As can be seen, the substituent effects on the reduction

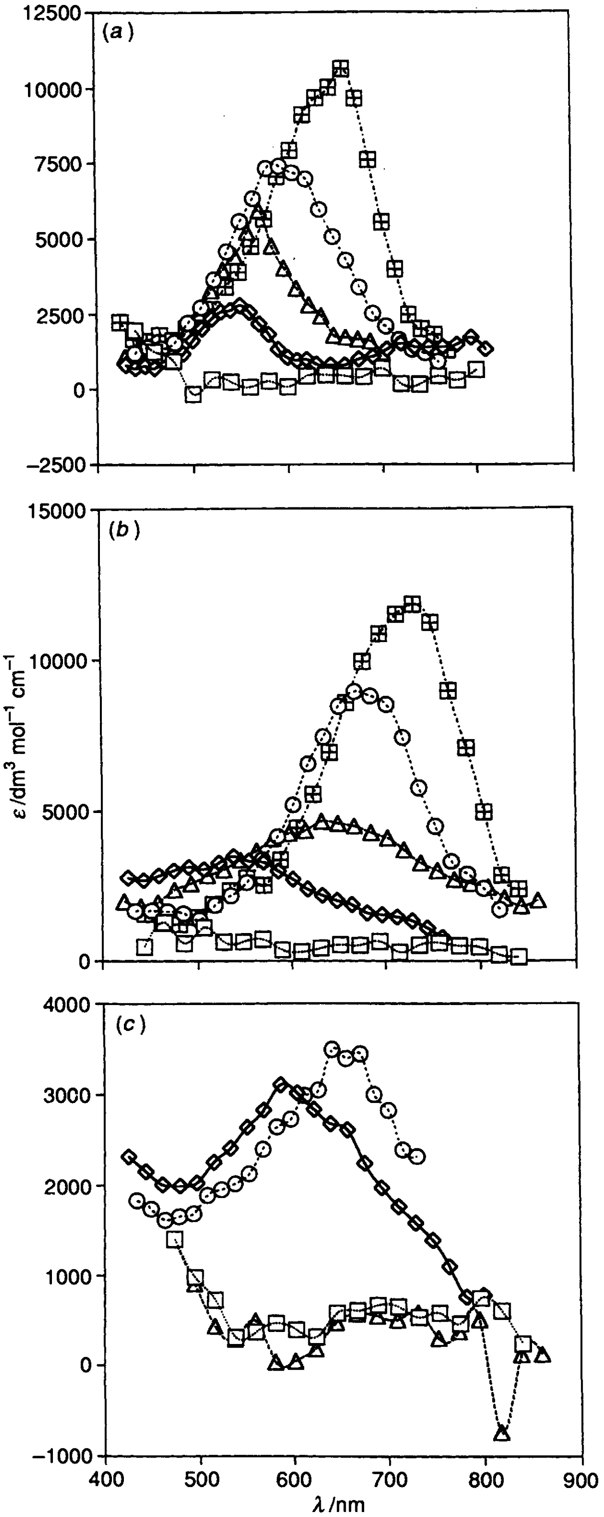

Fig. 1 Optical spectra of (*a*) 4-substituted aryl methyl sulfide radical cations, (*b*) 4-substituted aryl methyl selenide radical cations and (*c*) 4-substituted aryl methyl telluride radical cations $N(CH_3)_2$ (⊞), CH_3O (○), CH_3 (△), H (◇) and CF_3 (□)

potentials going from CH_3O– to CF_3– are very small for all three types of chalcogenides ($\rho^+ \approx 0.02$). In contrast, substituent effects predicted from eqn. (1) are much larger ($\rho^+ \approx 0.56$ for 4-R–C_6H_4–S–$CH_3{}^{\bullet +}$). Furthermore, the slopes do not differ significantly between S-, Se- and Te-containing compounds. However, $(CH_3)_2N$-substituted aryl methyl sulfide and selenide deviate markedly from the general trend, which can be understood from the nature of the radical cations. If the substituent is strongly electron donating the radical cation can be looked upon as a CH_3X-substituted benzene radical cation rather than an aryl methyl chalcogenide radical cation, *i.e.* the reduction potential of the substituted benzene radical cation is lower than that of the chalcogenide radical cation.

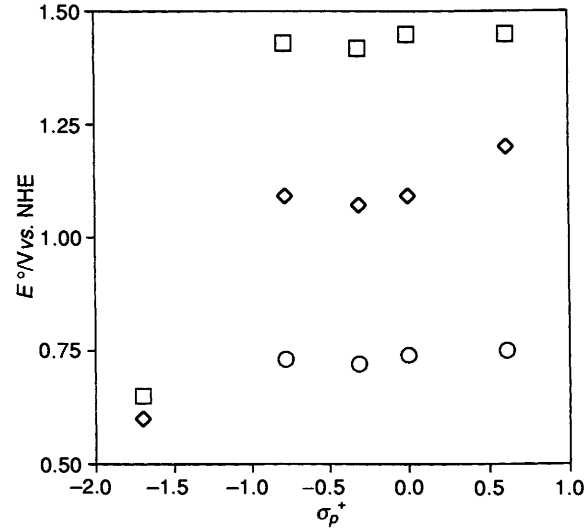

Fig. 2 One-electron reduction potentials of 4-substituted aryl methyl sulfide (□), selenide (◇) and telluride (○) radical cations as a function of the Brown σ_p^+ substituent constants

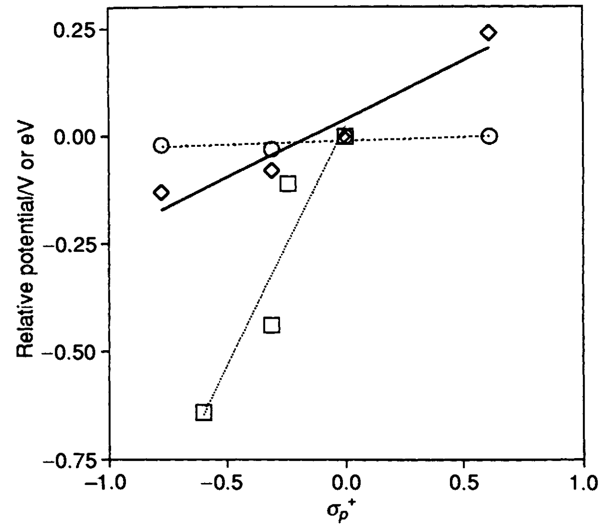

Fig. 3 Relative one-electron reduction potentials (○), peak oxidation potentials (◇) and gas-phase ionization energies (□) of 4-substituted aryl methyl sulfides as a function of the Brown σ_p^+ substituent constants

Electrochemical measurements of the peak oxidation potentials of 4-substituted aryl methyl chalcogenides in CH_3CN show the same trend, *i.e.* very small substituent effects going from the CH_3O- to the CF_3-substituent and markedly deviating potentials for the $(CH_3)_2N$-substituted aryl methyl chalcogenides.[1] The peak oxidation potentials of 4,4′-substituted diaryl chalcogenides show a similar trend indicating a change in nature of the radical cation when the electron-donating effect of the 4,4′-substituents becomes sufficiently large.[5]

In order to elucidate the rather weak substituent dependence on the one-electron reduction potentials of aryl methyl chalcogenide radical cations we have compared the reduction potentials measured in water, the peak oxidation potentials measured in acetonitrile and the gas-phase ionization energies.[16] In Fig. 3 we have plotted the relative (to the unsubstituted aryl methyl sulfide) values of the corresponding potentials of some 4-substituted aryl methyl chalcogenides

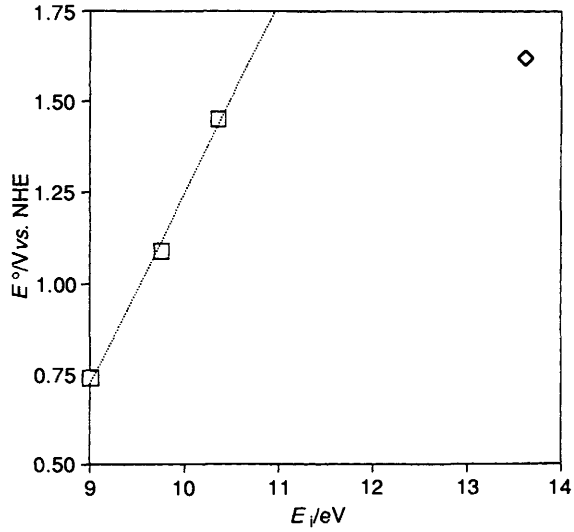

Fig. 4 One-electron reduction potentials of (from left to right) $(C_6H_5\text{-Te-}CH_3)^{\bullet+}$, $(C_6H_5\text{-Se-}CH_3)^{\bullet+}$, $(C_6H_5\text{-S-}CH_3)^{\bullet+}$ and $(C_6H_5\text{-O-}CH_3)^{\bullet+}$ as a function of the ionization energy of the heteroatom

against the Brown σ_p^+-constants. As can be seen, the effect of the substituent on the potential decreases markedly with increasing the polarity of the solvent. This can be understood in terms of solvation. Clearly, the more electron withdrawing the substituent, the stronger the radical cation is solvated in a polar solvent. In other words, the charge is more localized to the chalcogenide the more electron withdrawing is the substituent. This can also be seen when comparing the spectral properties of the radical cations, as was previously discussed.

It would then seem that to synthesize a better antioxidant by incorporating electron-donating substituents into aryl methyl chalcogenides or diaryl chalcogenides, may not meet with success, unless the drug is meant to function in a non-polar environment.

It is also interesting to compare the one-electron reduction potentials of unsubstituted aryl methyl chalcogenides with each other. In Fig. 4 we have plotted the reduction potentials of $(C_6H_5\text{-S-}CH_3)^{\bullet+}$, $(C_6H_5\text{-Se-}CH_3)^{\bullet+}$ and $(C_6H_5\text{-Te-}CH_3)^{\bullet+}$ against the ionization energies of S, Se and Te.[16] Oxygen is also included in the plot, to be discussed further on. As can be seen, the reduction potential of the radical cation is directly proportional to the ionization energy of the corresponding chalcogenide for S, Se and Te. This strongly indicates that the position of oxidation is at the chalcogenide atom. The anisole radical cation deviates markedly from the general trend, which can be accounted for by the high ionization energy of the oxygen atom. Owing to CH_3O-substitution the reduction potential of the benzene ring is sufficiently lowered for the oxidation to take place at the benzene ring rather than at the oxygen atom. Thus, the radical is to be regarded as a MeO-substituted benzene radical cation rather than an aryl methyl oxide radical cation.

One-electron Reduction Potentials of Organic Sulfide and Selenide Radical Cations.—The reduction potentials of $(CH_3)_2S^{\bullet+}$, $(C_6H_5)_2S^{\bullet+}$ and $C_6H_5\text{-S-}CH_3^{\bullet+}$ are 1.68,[5] 1.54[5] and 1.45 V *vs.* NHE, respectively. In the gas phase the corresponding ionization energies are 8.69, 7.86 and 7.94 eV, respectively.[16] As can be seen, the trend is not the same in the gas phase as in the aqueous phase, which could be accounted for by solvation effects in the latter case. However, the gas-phase ionization energies of the corresponding selenides are 8.40, 7.79 and 7.4 eV, respectively.[16] The trend is the same as for the one-electron reduction potentials of sulfide radical cations in water. In the aqueous phase, the one-electron reduction potentials of $(C_6H_5)_2Se^{\bullet+}$ and $C_6H_5\text{-Se-}CH_3^{\bullet+}$ are 1.37[5] and 1.09 V *vs.* NHE, respectively. The difference between these two potentials, 0.28 V, is significantly larger than the difference between the corresponding sulfides, 0.09 V. The difference between the highest and the lowest ionization energy is approximately equal for both sulfides and selenides, ≈ 1 eV. In view of these data we speculate that the ionization energy value of $(C_6H_5)_2S$ might be in error.

Without invoking any possible effects of solvation we believe that the trend methyl methyl, aryl aryl and aryl methyl chalcogenide can be explained by the chalcogenide being able to fully interact only with one aryl group, as the phenyl rings are not in the same plane. If one phenyl group in a diaryl chalcogenide is replaced by an electron-donating methyl group, the effects of the two groups will be synergistic. The chalcogen atom will be more electron rich and thus easier to oxidize and the corresponding radical cation will be resonance-stabilized by the phenyl group. In the case of dimethyl chalcogenides the chalcogenide will probably be even more electron rich. However the charge on the corresponding radical cation is not delocalized and therefore it is not resonance stabilized.

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