Redox Properties of Diaryl Chalcogenides and Their Oxides

Lars Engman, Johan Lind, and Gábor Merényi*

Laboratories of Organic and Nuclear Chemistry, Department of Chemistry, Royal Institute of Technology, S-10044 Stockholm, Sweden

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The redox properties of diaryl chalcogenides and their corresponding oxides were studied by means of pulse radiolysis. Diaryl sulfides, selenides, and tellurides were found to be readily ($k = 10^9$–10^{10} M^{-1} s^{-1}) oxidized to the corresponding radical cations by a variety of one-electron oxidants (Tl^{2+}, $OH^\bullet$, $Br_2^{\bullet-}$, $N_3^\bullet$). None of the radical cations appeared to form three-electron-bonded dimers with their corresponding chalcogenides. The radical cations of diaryl chalcogenides were also formed by one-electron reduction of their respective oxides. Among one-electron reductants tested, only the solvated electron was able to rapidly ($k = (0.9$–$2) \times 10^{10}$ M^{-1} s^{-1}) reduce diphenyl sulfoxide and diphenyl selenoxide between pH 3 and 13. Diphenyl telluroxide is present predominantly as a hydrate, $(C_6H_5)_2Te(OH)_2$, which undergoes protonation/dehydration below pH 5.3 to yield $(C_6H_5)_2TeOH^+$. Both of these species react rapidly with the solvated electron to yield the radical cation, but only $(C_6H_5)_2TeOH^+$ reacts with $CO_2^{\bullet-}$ with a measurably fast rate ($k = 6 \times 10^9$ M^{-1} s^{-1}). Upon one-electron oxidation, bis(4-hydroxymethyl) sulfide (pH > 0.5) and bis(4-hydroxyphenyl) telluride (pH > 2.5) were found to readily deprotonate to form phenoxyl radicals. Below pH 2.5, it was also possible to observe the radical cation spectrum of the organotellurium compound. One-electron reduction potentials of a variety of diaryl chalcogenide radical cations in water were obtained by bringing the chalcogenides to react with redox standards and by observing their redox equilibria by pulse radiolysis. The following $E°$ values versus NHE were determined: $E°((C_6H_5)_2S^{\bullet+}/(C_6H_5)_2S) = 1.54$ V; $E°((C_6H_5)_2Se^{\bullet+}/(C_6H_5)_2Se) = 1.37$ V; $E°((C_6H_5)_2Te^{\bullet+}/(C_6H_5)_2Te) = 1.14$ V; $E°((4\text{-HO–}C_6H_4)_2Te^{\bullet+}/(4\text{-HO–}C_6H_4)_2Te) = 0.95$ V; $E°((4\text{-}H_2N\text{–}C_6H_4)_2Te^{\bullet+}/(4\text{-}H_2N\text{–}C_6H_4)_2Te) = 0.80$ V; $E°((4\text{-}^-OOCCH_2O\text{–}C_6H_4)_2S^{\bullet+}/(4\text{-}^-OOCCH_2O\text{–}C_6H_4)_2S) = 1.21$ V. The two-electron redox potentials of the telluroxide/telluride redox couple were determined by means of EMF titration as a function of the pH. A value of 0.65 V was obtained for both the $((4\text{-HO–}C_6H_4)_2Te(OH)_2,2H^+)/((4\text{-HO–}C_6H_4)_2Te,2H_2O)$ and the $((4\text{-}H_2N\text{–}C_6H_4)_2Te(OH)_2,2H^+)/((4\text{-}H_2N\text{–}C_6H_4)_2Te,2H_2O)$ couples. The chalcogen–oxygen single-bond strengths in the OH adducts to diaryl chalcogenides were found to increase as one traverses the chalcogens from sulfur to tellurium. This is in contrast to the trend for the corresponding chalcogen–oxygen double bond strengths. A dissociation enthalpy of 84 kcal/mol was estimated for the Te=O bond in diaryl telluroxides. Calculated one-electron reduction potentials for diphenyl sulfoxide and dimethyl sulfoxide did not provide a thermodynamic rationale for the low reactivity of dialkyl sulfoxides toward the hydrated electron. Finally, the $(C_6H_5)_2S^{\bullet+}$ radical cation was produced by reduction of $(C_6H_5)_2SO$ in a 50/50 v/v water/*tert*-butyl alcohol mixture. We thus propose $(C_6H_5)_2S^{\bullet+}$ as a useful one-electron oxidant in mixed solvents.

Introduction

In contrast to a large amount of information available for dialkyl sulfur(III) radicals[1-8] in water, physicochemical data on corresponding diaryl species are lacking. This is also true in the case of the selenides/selenoxides and telluride/telluroxides. The present work is an attempt at remedying this flaw by providing basic physicochemical data for diaryl sulfides, selenides and tellurides and their corresponding oxides. The experimental method of choice is pulse radiolysis, as it has repeatedly proven its worth in providing reliable thermodynamic redox potentials for transient radicals[9] in cases where more traditional electrochemical techniques only can deliver estimates or trends at best. In the present work, the reactivity of radicals obtained as a result of one-electron oxidation of diaryl sulfides, selenides, and tellurides or, alternatively, the one-electron reduction of diaryl sulfoxides, selenoxides, and telluroxides will be described.

Results and Discussion

Radical Cations of Diphenyl Sulfide, Selenide, and Telluride. Diphenyl sulfide was oxidized by Tl^{2+} at pH 3.7 to yield a species characterized by the fully drawn spectrum in Figure 1. To test whether one-electron reduction of diphenyl sulfoxide would yield the same species the hydrated electron was brought to react with the latter. As can be gleaned from Figure 1, the species thus produced is indistinguishable from the one obtained through oxidation of the sulfide. Furthermore, its yield is invariant with the pH. The peaks at 360 and 750 nm are characteristic of the radical cation $(C_6H_5)_2S^{\bullet+}$, recently observed[10] in 1,2-dichloroethane. Kinetically, $(C_6H_5)_2S^{\bullet+}$ arises subsequent to reaction

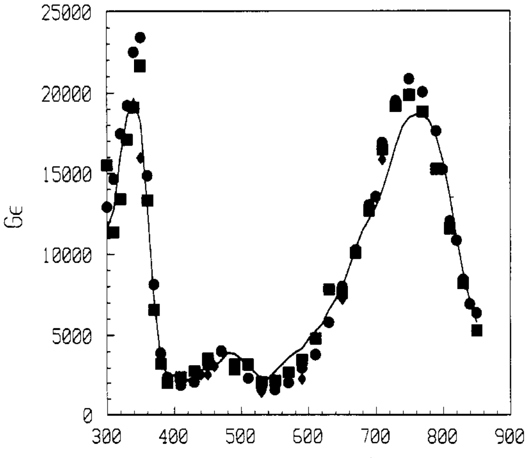

Figure 1. Transient spectra of $(C_6H_5)_2S^{\bullet+}$. Data obtained upon irradiation of argon-purged solutions containing 10^{-3} M $(C_6H_5)_2SO$ and 1 M 2-methyl-2-propanol are marked by points: (●) pH 7; (◆) pH 4.6; (■) pH 13. The full line represents the transient spectrum obtained upon irradiation of N_2O-saturated solutions at pH 3.7 containing 3×10^{-5} M $(C_6H_5)_2S$ and 10^{-3} M Tl_2SO_4.

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1, with a rate proportional to the concentration of the parent sulfide.

$$(C_6H_5)_2S + Tl^{2+} \rightleftharpoons (C_6H_5)_2S^{\bullet+} + Tl^{+} \qquad (1)$$

$$(C_6H_5)_2SO + e_{aq}^{-} \rightleftharpoons (C_6H_5)_2SO^{\bullet-} \qquad (2)$$

$$(C_6H_5)_2SO^{\bullet-} + H_2O \rightleftharpoons (C_6H_5)_2SOH^{\bullet} + OH^{-} \qquad (3)$$

$$(C_6H_5)_2SOH^{\bullet} \rightleftharpoons (C_6H_5)_2S^{\bullet+} + OH^{-} \qquad (4)$$

$$(C_6H_5)_2S^{\bullet+} + H_2O \rightleftharpoons (C_6H_5)_2SOH^{\bullet} + H^{+} \qquad (5)$$

Alternatively, $(C_6H_5)_2S^{\bullet+}$ is formed without delay in reactions 2–4 with a rate proportional to the concentration of $(C_6H_5)_2SO$. At $[(C_6H_5)_2SO] > 5 \times 10^{-3}$ M the radical cation appears with a rate $>10^7$ s^{-1}, the time resolution of the instrument.

This finding reveals that both protonation of $(C_6H_5)_2SO^{\bullet-}$ by H_2O to form the neutral radical $(C_6H_5)_2SOH^{\bullet}$ (eq 3) as well as the expulsion of OH^- from the latter (eq 4) must occur with a rate larger than 10^7 s^{-1}. Setting 10^{10} M^{-1} s^{-1} as the upper limit to the rate constant of deprotonation of $(C_6H_5)_2SOH^{\bullet}$ by OH^-, we derive $pK_a((C_6H_5)_2SOH^{\bullet}) = pK_w + \log K(3) > 11$. From the pH independence of the cation yield it follows that up to at least pH 14 the radical cation does not hydrolyze to form a pseudobase radical. In fact, as the size of the $(C_6H_5)_2S^{\bullet+}$ absorbance at 750 nm observed at pH 14 differs by less than 10% from that seen at lower pH, K_4 must be larger than 10 M or $(pK_a)_5 > 15$.

As to extinction coefficients, in O_2-saturated Tl^+ solutions containing $(C_6H_5)_2S$ at pH 2, where the G value of $(C_6H_5)_2S^{\bullet+}$ should be 2.8, the extinction coefficient at 750 nm is calculated to be 7000 M^{-1} cm^{-1}. This value is also arrived at in N_2O-saturated Br^- solutions, if $G(Br_2^{\bullet-}) = 5.4$ is taken. An identical extinction coefficient is obtained from $G\epsilon$ according to reaction 2, assuming 2.8 as the G value of the hydrated electron, e_{aq}^-. In Figure 1 the oxidation reaction 1 was carried out in N_2O saturated solution at pH 3.7, at which pH Tl^{2+} hydrolyzes[11] to about 10% according to reaction 6. The figure reveals that the observed yield of

$$Tl^{2+} + OH^{-} \rightleftharpoons Tl(OH)^{+} \qquad (6)$$

$(C_6H_5)_2S^{\bullet+}$ is only ca. half of that expected during the oxidation of the sulfide by Tl^{2+}. The lower yield presumably hinges on the presence of $Tl(OH)^+$. The radical cation $(C_6H_5)_2S^{\bullet+}$ formed in reactions 2–4 was found to decay with first-order kinetics and the rate was proportional to the concentration of the parent $(C_6H_5)_2SO$ ($k \approx 10^8$ M^{-1} s^{-1}). This behavior could be due to addition of the radical cation to the sulfoxide, presumably at the para position, similarly to the process discussed in ref 12. The rate of radical decay also appeared to increase with increasing OH^- concentration (apparent $k \approx 10^6$ M^{-1} s^{-1}). This feature cannot be due to the reverse of eq 4, given the fact that the radical cation accumulates prior to consumption. A possible reaction might be the addition of OH^- to the aromatic ring. We note, however, that the presence of no more than 1% of CO_3^{2-} in the hydroxide would suffice to cause the observed decay by electron transfer from CO_3^{2-} to $(C_6H_5)_2S^{\bullet+}$.

Figure 2 presents the spectra of the corresponding telluride and selenide radical cations, $(C_6H_5)_2Te^{\bullet+}$ and $(C_6H_5)_2Se^{\bullet+}$. While the extinction coefficient of the selenide cation is comparable to that of the sulfide cation, the telluride cation absorbs appreciably weaker over the whole spectral range. As with diphenyl sulfide, the radical cations of diphenyl selenide and telluride are formed with identical yields, irrespective of whether they are produced by one-electron oxidation of the chalcogenide or by one-electron reduction of the corresponding oxide. Also, around pH 7, protonation of the one-electron reduced diaryl selenoxide/telluroxide and subsequent OH^- expulsion from the neutral pseudobase radical to yield the chalcogenide radical cation occurs well within 1 μs. The selenide species was accorded only cursory attention as to its pH behavior. At pH 13 the absorbance at 710 nm of the radical cation appeared to be reduced to ca. half its value at neutral pH:

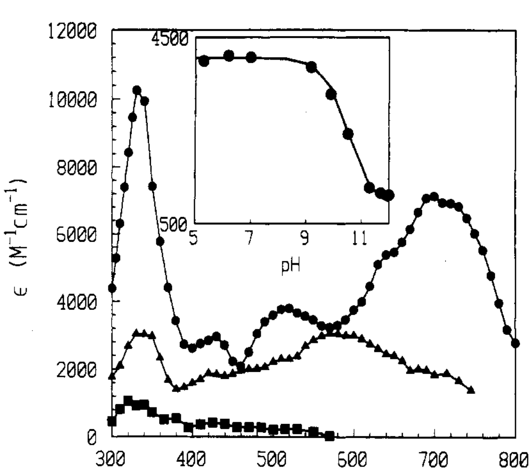

Figure 2. Transient spectra: (●) Irradiation of neutral argon purged solutions containing 10^{-3} M $(C_6H_5)_2SeO$ and 1 M 2-methyl-2-propanol. (▲) Irradiation of argon-purged solutions at pH 5 containing 10^{-3} M $(C_6H_5)_2TeO$ and 1 M 2-methyl-2-propanol. (■) Irradiation of a N_2O saturated solutions at pH 12 containing 3×10^{-5} M $(C_6H_5)_2Te$ and 10^{-3} M N_3^-. Insert: Absorbance at 560 nm vs pH when N_2O-saturated solutions containing 3×10^{-5} M $(C_6H_5)_2Te$ and 10^{-3} M N_3^- were irradiated. The line in the insert is calculated with a pK_a of 10.3.

$$(C_6H_5)_2Se^{\bullet+} + H_2O \rightleftharpoons (C_6H_5)_2SeOH^{\bullet} + H^{+} \qquad (7)$$

In view of this we set $pK_a(7) \geq 13$. However, in the absence of a systematic pH titration this value remains provisional. In the case of the corresponding telluride radical cation a clear hydrolysis equilibrium could be observed. This is reflected in the inset of Figure 2, which depicts the variation of the extinction coefficient at 550 nm as a function of the pH. As can be seen, $pK_a(8) = 10.3$ is obtained. Actually, as will be discussed further on, it is more correct to say that $pK_a(8) \geq 10.3$:

$$(C_6H_5)_2Te^{\bullet+} + H_2O \rightleftharpoons (C_6H_5)_2TeOH^{\bullet} + H^{+} \qquad (8)$$

Figure 2 also reveals that $(C_6H_5)_2TeOH^{\bullet}$ is essentially transparent in the spectral range presented.

Table 1 collects rate constants of the diaryl chalcogenides reacting with a number of one-electron oxidants. These comprise Tl^{2+}, $N_3^{\bullet}$, $Br_2^{\bullet-}$, and $OH^{\bullet}$. Some comments should perhaps be made on the last oxidant. Its reaction with the chalcogenides yields radical cations with less than quantitative yield, the latter varying with the chalcogenide. Thus at pH 7, ca. 50% $(C_6H_5)_2S^{\bullet+}$ but more than 90% $(C_6H_5)_2Te^{\bullet+}$ is produced with $OH^{\bullet}$. The radical cation yield increases somewhat with decreasing pH. It would seem that hydroxyl radicals partly undergo addition to the aromatic ring, followed by proton-catalyzed dehydration. The prompt formation of the radical cation probably involves initial formation of the pseudobase radical followed by OH^- expulsion in a non-rate-determining step.

It was also found that the spectral shapes and sizes of chalcogenide radical cations remained unaffected when the concentration of the parent chalcogenide varied up to the solubility limit. This shows that, at least in the investigated concentration range, no radical dimer cations form via three-electron bonds. This observation also holds for substituted diaryl chalcogenides (to be treated below) which are sufficiently soluble (up to 0.01 M or so). Recalling that for dialkyl sulfide radical cations very strong dimer complexes have been reported,[7] we conclude that the aryl groups strongly stabilize the positive charge via resonance.

TABLE 1: Rate Constants Determined in This Work

reaction	rate constant (M^{-1} s^{-1})	wavelength[a] (nm)
$e^-_{aq} + (C_6H_5)_2SO$	9.1×10^9	decay 650
$e^-_{aq} + (4\text{-}O^-\text{-}C_6H_4)_2SO$	$7.5 \times 10^{8}9$	decay 650
$e^-_{aq} + (t\text{-}C_4H_9)_2SO$	1.5×10^7	decay 650
$e^-_{aq} + (n\text{-}C_4H_9)_2SO$	3.7×10^6	decay 650
$e^-_{aq} + (C_6H_5)_2SeO$	2×10^{10}	decay 650
$e^-_{aq} + (C_6H_5)_2Te$	2×10^{10}	decay 650
$e^-_{aq} + (C_6H_5)_2TeOH^+$	3.7×10^{10}	decay 650
$e^-_{aq} + (C_6H_5)_2Te(OH)_2$	1.5×10^{10}	decay 650
$CO_2^{\bullet-} + (C_6H_5)_2SeO$	$<10^8$	pbk 750
$CO_2^{\bullet-} + (C_6H_5)_2TeOH^+$	6×10^9	pbk 580
$CO_2^{\bullet-} + (C_6H_5)_2Te(OH)_2$	$<10^8$	pbk 580
$CO_2^- + (4\text{-}H_2N\text{-}C_6H_4)_2TeOH^+$	5.5×10^9	pbk 780
$(CH_3)_2(OH)C^\bullet +$ $(4\text{-}HO\text{-}C_6H_4)_2TeOH^+$	4×10^8	pbk 750
$OH^\bullet + (C_6H_5)_2S$	1.3×10^{10}	pbk 750
$OH^\bullet + (C_6H_5)_2Se$	1.1×10^{10}	pbk 750
$OH^\bullet + (C_6H_5)_2Te$	1.3×10^{10}	pbk 580
$OH^\bullet + (4\text{-}H_2N\text{-}C_6H_4)_2Te$	1.1×10^{10}	pbk 780
$Tl^{2}+ + (C_6H_5)_2S$	3×10^9	pbk 750
$Tl^{2+} + (C_6H_5)_2Se$	2.6×10^9	pbk 750
$Tl^{2+} + (C_6H_5)_2Te$	3.2×10^9	pbk 580
$Br_2^{\bullet-} + (C_6H_5)_2S$	1.4×10^9	pbk 750
$Br_2^{\bullet-} + (C_6H_5)_2Se$	2.8×10^9	pbk 750
$Br_2^{\bullet-} + (C_6H_5)_2Te$	3.5×10^9	pbk 580
$Br_2^{\bullet-} + (4\text{-}H_2N\text{-}C_6H_4)_2Te$	6×10^9	pbk 780
$N_3^\bullet + (C_6H_5)_2Te$	5.0×10^9	pbk 580
$N_3^\bullet + (4\text{-}H_2N\text{-}C_6H_4)_2Te$	8.8×10^9	pbk 780
$N_3^\bullet + (4\text{-}HO\text{-}C_6H_4)_2Te$	9.7×10^9	pbk 750
$(C_6H_5)_2S^{\bullet+} +$ 1,3-dimethoxybenzene	2×10^9	decay 750 nm
$(C_6H_5)_2S^{\bullet+} + N_3^-$	6.1×10^9	decay 750 nm
$(C_6H_5)_2S^{\bullet+} + CO_3^{2-}$	1.8×10^8	decay 750 nm

[a] pbk is the abbreviation for product buildup kinetics.

This is in keeping with the strong visible absorption of $(C_6H_5)_2S^{\bullet+}$ as compared with the rather uncoloured $(CH_3)_2S^{\bullet+}$.

Kinetics of Reduction of Diphenyl Sulfoxide, Selenoxide, and Telluroxide. From Table 1 it transpires that the hydrated electron reacts with $(C_6H_5)_2SO$ with an essentially diffusion controlled rate. This is somewhat surprising, as the corresponding alkyl variant, $(CH_3)_2SO$ (DMSO), reacts very slowly[1] ($k = 1.6 \times 10^6$ M^{-1} s^{-1}). We could also confirm that this rate remains slow if $(CH_3)_2SO$ is interchanged for $(C(CH_3)_3)_2SO$ or $(C_4H_9)_2SO$ (see Table 1). It has been reported[13] that while the latter compound gives rise to a catalytic hydrogen wave at the electrodes, the former two are electrode-inactive. The data in Table 1 provide no explanation for this observation, i.e., the reaction rate of the hydrated electron does not reflect the reported electrochemical properties of dialkyl sulfoxides. We believe the difference in electrode reducibility of alkyl sulfoxides to derive from different degrees of adsorption at the cathode surface. We shall later discuss the possible reasons for the difference in reactivity of dialkyl and diaryl sulfoxides toward the hydrated electron. As transpires from Table 1, both $(C_6H_5)_2SO$ and $(C_6H_5)_2SeO$ react with similar and very fast rates with the hydrated electron. Furthermore, the rate of electron reduction of these two oxides was found independent of the pH between pH 3 and 13. Equally important, the hydrated electron produces the corresponding radical cation (see above) at all pH values. In contrast to the rapid and unique reaction of sulfoxide and selenoxide with e_{aq}^- no other one-electron reductants tested were found to react with measurable rates. The rate constants between $CO_2^{\bullet-}$ and these oxides in Table 1 are upper limits, but the actual rates may be much lower than that.

The behavior of $(C_6H_5)_2TeO$ is somewhat different. Although it yields the radical cation quantitatively up to pH 10 (above which the latter hydrolyzes, *vide supra*), the rate constant is lowered above pH 6 to attain a value ca. 40% of that at low pH. As can be seen in Table 1, the high pH rate is about the same as the corresponding rate constant of e_{aq}^- reacting with the diaryl telluride, $(C_6H_5)_2Te$, through dissociative electron transfer.[14] These observations suggest a protonation/hydration equilibrium according to eq 9. Such an equilibrium has previously been

$$(C_6H_5)_2TeOH^+ + H_2O \rightleftharpoons (C_6H_5)_2Te(OH)_2 + H^+ \quad (9)$$

proposed[15] for dialkyl telluroxides. The protonated telluroxide was found to react rapidly with both $CO_2^{\bullet-}$ (see Table 1) and $(CH_3)_2(OH)C^\bullet$. On the other hand no reaction of $(C_6H_5)_2Te(OH)_2$ could be observed with any of these reductants. Equilibrium 9 was studied spectrophotometrically by varying the pH between 2 and 8 and measuring the absorbance of dissolved (10^{-4} M) diphenyltelluroxide at several wavelengths. At 22.3 °C and an ionic strength <0.01 M, $pK_a(9) = 5.3 \pm 0.2$ was obtained. We note that this value is not far from 6, the reported[15] pK_a of $(CH_3)_2TeOH^+$. Protonation of $(C_6H_5)_2SO$ occurs[16] around pH −2.5, and that of $(C_6H_5)_2SeO$ is expected to take place below pH 2.

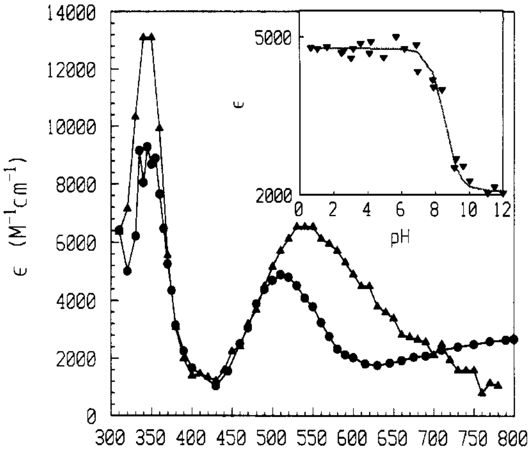

Figure 3. Transient spectra obtained from $(4\text{-}OH\text{-}C_6H_5)_2S$. (▲) Irradiation of aerated solutions at pH 1 containing 0.3 mM $(4\text{-}OH\text{-}C_6H_5)_2S$ and 5 mM Tl_2SO_4. (●) Irradiation of aerated solutions at pH 11 containing 0.3 mM $(4\text{-}OH\text{-}C_6H_5)_2S$ and 10 mM N_3^-. Insert: pH profile of the absorbance at 600 nm. Primary oxidants were $Br_2^{\bullet-}$, $N_3^\bullet$ (pH > 6) and Tl^{2+} (pH < 2). The full line is calculated using a pK_a of 8.5.

One-Electron Oxidation of 4,4′-Disubstituted Diaryl Chalcogenides. If diaryl chalcogenides are substituted with electron-releasing groups, they can be regarded as bifunctional as far as redox centers are concerned. We have investigated the effects of OH and NH_2 substitution in the 4,4′-positions. In principle, the radical cation generated from such compounds is a delocalized hybrid cation. However, depending on the redox and spectral properties of the isolated functional groups (e.g., unsubstituted chalcogenide vs unsubstituted phenol), the properties of the actual species may vary between the two extremes. In addition, given the possibility of proton loss from the functional group of the radical cation, the spectral and redox properties of such species may display interesting and enlightening changes with the pH.

Bis(4-hydroxyphenyl) Sulfide. Figure 3 displays the spectra of one-electron oxidized $(4\text{-}HO\text{-}C_6H_4)_2S$ at two pH values. The two spectra show a similarity but still differ significantly. The inset shows a pH titration where a sigmoid curve typical of a pH-dependent interconversion of two species is observed. As is indicated in the legend, the extinction coefficients were calculated by scaling the absorbance with the appropriate radiation chemical G value (2.8 for Tl^{2+} in O_2-saturated Tl^+ solutions between pH 0.5 and 2, and 5.4 for $Br_2^{\bullet-}$ and $N_3^\bullet$, respectively, in N_2O-saturated Br^- solutions between pH 2 and 6 or in N_3^- solutions above pH 6). In this broad pH interval $pK_a = 8.5$ is observed. As such a sigmoid curve is not seen with $(C_6H_5)_2S^{\bullet+}$, we must conclude that the observed pK_a is due not to pseudobase formation (see eq 5) but to deprotonation of a phenolic OH group. Now, both spectra of Figure 3 are seen to have absorption maxima in the visible that are shifted by 200–250 nm to shorter wavelengths

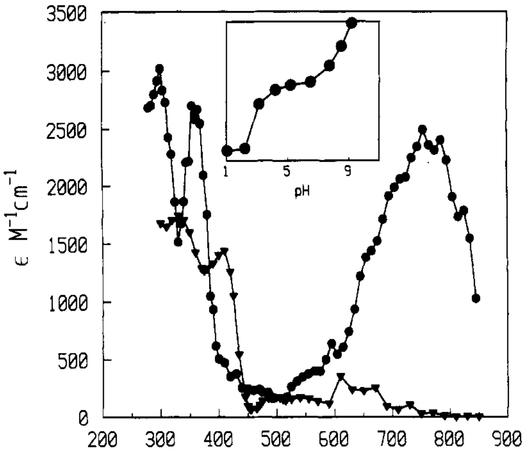

Figure 4. Transient spectra obtained from (4-OH–$C_6H_5)_2Te$. (▼) Irradiation of aerated solutions at pH 1 containing 0.3 mM (4-OH–$C_6H_5)_2Te$ and 5 mM Tl_2SO_4. (●) Irradiation of aerated solutions at pH 6.7 containing 0.3 mM (4-OH–$C_6H_5)_2Te$ and 10 mM N_3^-. Insert: pH profile of the absorbance at 750 nm obtained upon irradiation of aerated solutions containing Br^-.

with respect to the spectrum in Figure 1. Were the low-pH spectrum in Figure 3 to characterize the cation (4-OH–$C_6H_4)_2S^{\bullet+}$, one would have expected it to shift toward longer wavelengths as a result of charge delocalization. The finding that rather the opposite is true suggests that it belongs to a neutral radical, deprotonated at one OH group, i.e., a substituted phenoxyl radical (4-HO–C_6H_4)S(C_6H_4–4-$O^\bullet$). Apparently, the cation deprotonates above pH 0.5, the lowest pH considered. Such a high acidity is consistent with that of ordinary phenol radical cations, which are known[17] to have pK_a values well below 0.

The similarities of the high- and low-pH spectra can be understood in the light of structural considerations. For steric reasons the aryl groups in diaryl chalcogenides are generally not coplanar.[18] Therefore, the OH group in (4-HO–C_6H_4)S(C_6H_4–4-$O^\bullet$) should couple only weakly with the radical site. If this is the case, the OH group in (4-HO–C_6H_4)S(C_6H_4–4-$O^\bullet$) should deprotonate at a pH close to if somewhat lower than that of the parent (4-OH–$C_6H_4)_2S$. A pK_a of 8.5 is clearly close to ca. 10.4, the first pK_a of the parent,[19] supporting our assignment, namely, that the high-pH spectrum is due to the anionic phenoxyl radical (4-$^-$O–C_6H_4)S(C_6H_4–4-$O^\bullet$). In the sequel, we shall again touch on these points in the context of redox properties.

Bis(4-hydroxyphenyl) Telluride. Figure 4 displays the product of one-electron oxidation of bis(4-hydroxyphenyl) telluride. Here, we can observe a significant difference between the two spectra in the visible region. At pH 1 the spectral size above 450 nm is very small, and in this respect it resembles that of the unsubstituted $(C_6H_5)_2Te^{\bullet+}$ radical displayed in Figure 2 at neutral pH. Therefore, we ascribe this spectrum to (4-HO–$C_6H_4)_2Te^{\bullet+}$. The inset reveals at least two pK_a values, the first at ca. pH 2.5 and the second around 8–9. The first pK_a is surely due to formation of a neutral phenoxyl radical, while the second, which is close to the apparent pK_a = 8.5 of the corresponding sulfur analogue and also to that of the parent, probably characterizes deprotonation of the second OH group to form an anionic phenoxyl radical. The interesting observation is the relatively high value, ca. 2.5, of the first pK_a, which exceeds by over 3 units the usual pK_a values[17] of phenol radical cations. When learning more about the redox potentials, we shall attempt to rationalize this finding.

Bis(4-aminophenyl) Chalcogenides. Figure 5 displays the spectra of one-electron oxidized bis(4-aminophenyl) sulfide, selenide, and telluride, respectively, at pH 7. Just as with the unsubstituted analogues, one observes similar extinction coefficients for sulfide and selenide, while that for the telluride is considerably lower. Also, there is a monotonic shift to the red portion of the spectrum upon traversing the series from sulfide to telluride. In the case of the telluride, one observes a decrease of the spectral size in the red region when the pH is increased. This change is characterized by an apparent pK_a of 10.5. Well below pH 10 the redox potentials (details of their measurement will be described later) of the amino-substituted diaryl sulfides and tellurides were found invariant with the pH. From these observations we conclude that the spectra in Figure 5 pertain to radical cations. The above mentioned pK_a = 10.5 is within experimental error the same as that of the unsubstituted $(C_6H_5)_2Te^{\bullet+}$. Thus, we ascribe the change to hydrolysis of the cation, similar to eq 9. Apparently, the pK_a of pseudobase formation is essentially unaffected by the substituent. The deprotonation of the NH_2 group in the radical cation should then have a $pK_a >$ 10.5.

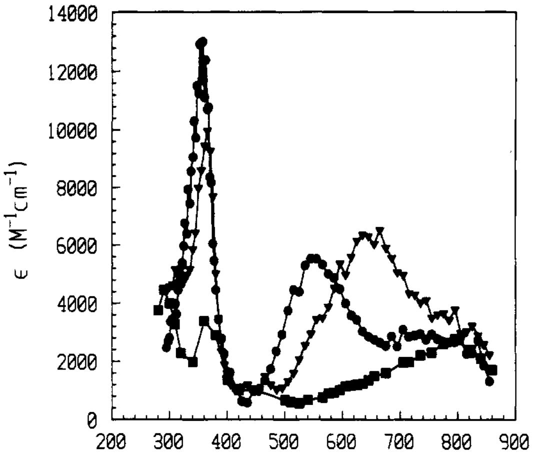

Figure 5. Transient spectra obtained upon pulsed irradiation. Conditions: N_2O saturation, pH 6.3, 10^{-4} M substrate, 10^{-2} M N_3^-. (●) (4-NH_2–$C_6H_4)_2S$; (▼) (4-NH_2–$C_6H_4)_2Se$; (■) (4-NH_2–$C_6H_4)_2Te$.

One-Electron Reduction Potentials of Diaryl Chalcogenide Radical Cations. To date a fair amount of electrochemically measured redox potentials, mostly in acetonitrile, have been reported[20,21] for diaryl and dialkyl sulfides. These are irreversible potentials and may vary by up to 300 mV between laboratories for a particular compound. To our knowledge the only comprehensive list of electrochemical potentials relating to selenides and tellurides has been published in ref 22. Although these reported values refer to irreversible potentials obtained by cyclic voltammetry in acetonitrile, they show a systematic trend. In addition, the data reveal a linear free energy relationship, where the potentials smoothly correlate with Brown σ^+_p values. This relationship is also expected to hold for truly thermodynamical redox potentials in water, although probably with different slopes. In the present work we shall equilibrate the diaryl chalcogenides with redox couples of well-known reduction potentials and from the redox equilibria observed within a short time span, on the order of a few microseconds, a thermodynamic reduction potential of the chalcogenide radical cation will be established. Before accounting for our results, it is worth mentioning that there are sufficient data in the literature to calculate the aqueous one-electron reduction potential of the much-studied $(CH_3)_2S^{\bullet+}/(CH_3)_2S$ couple.[1-7] From data in refs 5 and 6 where the equilibria (10)–(12) were determined by pulse radiolysis and utilizing $E°(Br_2^{\bullet-}/2\ Br^-)$ we calculate $E°((CH_3)_2S^{\bullet+}/(CH_3)_2S)$ = 1.68 V.

$$(CH_3)_2S^{\bullet+} + (CH_3)_2S \rightleftharpoons ((CH_3)_2S)_2^{\bullet+} \qquad (10)$$

$$(CH_3)_2S + Br_2^{\bullet-} \rightleftharpoons (CH_3)_2SBr^\bullet + Br^- \qquad (11)$$

$$(CH_3)_2SBr^\bullet + (CH_3)_2S \rightleftharpoons ((CH_3)_2S)_2^{\bullet+} + Br^{\bullet-} \qquad (12)$$

TABLE 2: One-Electron Reduction Potentials Derived from the Equilibria[a]

$$S + R^{+\bullet} \rightleftharpoons S^{+\bullet} + R \qquad K$$

substance (S)	reference (R)	K	$E°_{ref}$	E^0 (vs NHE)
$(C_6H_5)_2Te$[a]	1-methylindole	6.2	1.20[23]	1.15
$(C_6H_5)_2Te$[a]	N_3^-	3×10^3	1.33[24,25,26]	1.12
$(C_6H_5)_2Se$	veratrole	10 ± 2	1.44[27]	1.38
$(C_6H_5)_2Se$	1,4-dimethoxybenzene	0.1	1.30[27]	1.36
$(C_6H_5)_2S$	2 Br^-	30	1.63[28]	1.54
$(C_6H_5)_2S$	anisole	25	1.62[27]	1.54
$(C_6H_5)_2S$	CO_3^{2-}	4.5	1.59[29]	1.55
promethazine[b]	2,3-dimethylindole	2.2	0.93[30]	0.91
promethazine[c]	ClO_2^-	7.1	0.934[31]	0.88
promethazine[d]	$IrCl_6^{3-}$	3.7×10^{-2}	0.90[32]	0.98
$(4\text{-}HO\text{-}C_6H_4)_2Te$[e]	2,3-dimethylindole	0.5		0.95
$(4\text{-}HO\text{-}C_6H_4)_2Te$[e]	promethazine	0.23	0.91[33]	0.95
$(4\text{-}^-O_2CCH_2O\text{-}C_6H_4)_2S$	N_3^-	100		1.21
$(4\text{-}H_2N\text{-}C_6H_4)_2Te$[f]	4-iodophenol	8.6	$E_{9.1}$ 0.84[34]	0.78
$(4\text{-}H_2N\text{-}C_6H_4)_2Te$[g]	4-hydroxybenzoate	54.2	$E_{9.3}$ 0.92[34]	0.82

[a] Experiments were performed at (a) pH 7, (b) pH 4, (c) I(onic strength) = 10^{-2} M, (d) $I = 3 \times 10^{-2}$, (e) pH 1, (f) pH 9.1, (g) 9.3.

Table 2 compiles the redox couples and redox equilibria that were observed by means of pulse radiolysis. By employment of the previously established redox potentials of the reference couples, the thermodynamic one-electron reduction potentials vs NHE of the chalcogenides were arrived at. These are presented in the last column of the table. Whenever possible, the equilibrium constants were determined both directly and by studying the kinetics of equilibration as a function of reactant concentration. An example of these methods is illustrated in Figure 6. Here, the $(C_6H_5)_2S^{\bullet+}/(C_6H_5)_2S$ couple was brought to react with $Br_2^{\bullet-}/2Br^-$. We consider the global equilibrium:

$$Ph_2S + Br_2^{\bullet-} \rightleftharpoons Ph_2S^{\bullet+} + 2Br^- \qquad K = k_f/k_r$$

Then, at 730 nm, where only $Ph_2S^{\bullet+}$ absorbs, we obtain the equations

$$OD^{-1} = OD_0^{-1}(1 + [Br^-]^2/K[Ph_2S])$$

$$k_{obs} = k_f[Ph_2S] + k_r[Br^-]^2$$

Here, OD denotes the measured optical density, while OD_0 is its maximum value, i.e., when the equilibrium is completely driven to the right. The two ways yielded identical equilibrium constants. An interesting observation was the rate of equilibration being found proportional to the square of the Br^- concentration, i.e., the overall reaction was third order in reactants.

As the elementary step is unlikely to be termolecular, we suggest a very short-lived intermediate between the radical cation and Br^-, according to eqs 13 and 14. Steady-state treatment of

$$(C_6H_5)_2S + Br_2^{\bullet-} \rightleftharpoons (C_6H_5)_2SBr^\bullet + Br^- \qquad (13)$$

$$(C_6H_5)_2SBr^\bullet \rightleftharpoons (C_6H_5)_2S^{\bullet+} + Br^- \qquad (14)$$

$(C_6H_5)_2SBr^\bullet$ yields the observed concentration dependence as follows:

$$d[Ph_2S^{\bullet+}]/dt = k_{14}[(C_6H_5)_2SBr^\bullet] - k_{-14}[Br^-][Ph_2S^{\bullet+}]$$

$$d[(C_6H_5)_2SBr^\bullet]/dt = k_{13}[Ph_2S][Br_2^{\bullet-}] - (k_{-13}[Br^-] + k_{14})[(C_6H_5)_2SBr^\bullet] + k_{-14}[Br^-][Ph_2S^{\bullet+}] = 0$$

Solving for $[(C_6H_5)_2SBr^\bullet]$ and inserting the expression into the first equation we obtain, after setting $k_{14} \gg k_{-13}[Br^-]$:

$$d[Ph_2S^{\bullet+}]/dt = k_{13}[Ph_2S][Br_2^{\bullet-}] - k_{-13}K_{14}^{-1}[Br^-]^2[Ph_2S^{\bullet+}]$$

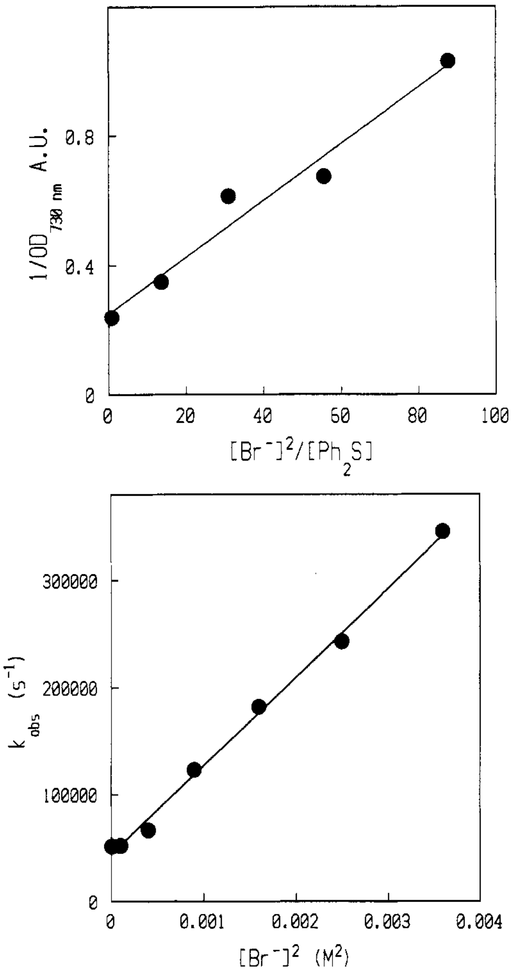

Figure 6. (a, top) Inverse of the optical density at 730 nm as a function of the ratio $[Br^-]^2/[(C_6H_5)_2S]$. (b, bottom) Observed first-order rate constant of equilibration versus $[Br^-]^2$. Conditions: neutral N_2O-saturated solutions; $[(C_6H_5)_2S]$ was varied between 2.5 and 3×10^{-5} M.

Identification with the above global equilibrium yields

$$k_f = k_{13} \qquad k_r = k_{-13}K_{14}^{-1}$$

We note that, unlike in water, $(C_6H_5)_2SBr^\bullet$ has been observed in halocarbons.[10] Furthermore, the occurrence of the alkyl analogue, $(CH_3)_2SBr^\bullet$, is well-established in water.[5]

The value of $E°((C_6H_5)_2S^{\bullet+}/(C_6H_5)_2S$ = 1.54 V has been determined against three references, namely, Br^-, CO_3^{2-}, and anisole. The latter two references, in turn, have been determined against Br^- as well. We thus have a very consistent set of determinations, which are ultimately based on $E^\circ(Br_2^{\bullet-}/2Br^-) = 1.63$ V vs NHE.[28] The E° value of $(CH_3)_2S$ is seen to exceed that of $(C_6H_5)_2S$ by merely 0.14 V. On the other hand the gaseous ionization potentials[35] of the two compounds differ by as much as 0.83 eV. Estimating from data in ref 36 $(C_6H_5)_2S$ to be solvated more strongly, by ca. 2 kcal/mol, than $(CH_3)_2S$, we calculate the free energy of hydration of $(CH_3)_2S^{\bullet+}$ to be more negative by 14 kcal/mol than that of $(C_6H_5)_2S^{\bullet+}$. This suggests a rather concentrated positive charge on the S atom in the alkyl compound, while in the diaryl variant the charge should be strongly delocalized over a phenyl ring. This state of affairs is also borne out by the optical absorbances of the two cations. Furthermore, the fact that $(CH_3)_2S^{\bullet+}$ readily forms a pseudobase radical[1] as well as adducts with dialkyl sulfides[6] or halide ions,[5] while none of these complexes could be observed with $(C_6H_5)_2S^{\bullet+}$ even in the most extreme of conditions, strongly emphasizes these structural differences.

As can be seen in Table 2, the E° values of the three unsubstituted diphenyl chalcogenides are rather evenly spaced, with ca. 200 mV between them. The redox potentials of some 4,4′-disubstituted chalcogenide radical cations have also been determined. As was mentioned above, the bis(4-hydroxyphenyl) sulfide radical cation deprotonates with a $pK_a < 0.5$. Hence its E° could not be determined. Instead, we chose bis[(4-carboxymethoxy)phenyl] sulfide, which is water soluble as a carboxylate and a good model of bis(4-methoxyphenyl) sulfides. The substituent lowers the E° value by 0.33 V as compared to the unsubstituted sulfide. In ref 22 a good correlation between E° values of chalcogenides and Brown σ^+_p values was demonstrated. From this correlation an approximate value of 1.15 V is predicted for the bis(4-hydroxyphenyl) sulfide radical cation. On the other hand, the redox potentials of substituted phenoxyl radicals were shown in refs 22 and 37 to also nicely correlate with σ^+_p values. The σ^+_p value of the 4-HO–C_6H_4–S substituent should be more negative than −0.55, the reported[38] σ^+_p for C_6H_5S. Utilizing eq 15, derived in ref 37, we obtain 0.60 V as the maximum

$$E^\circ = 0.79 + 0.34\sigma^+_p \qquad (15)$$

value for E°(phenoxyl radical/phenolate). As the pK_a of the parent phenol is 10.3, we calculate the pK_a of $(4\text{-HO–}C_6H_4)_2S^{\bullet+}$ to be below 1. This is in keeping with our failure to observe the cation above pH 0.5.

In the case of the corresponding hydroxy-substituted tellurium compound the radical cation is considerably less acidic. Utilizing the observed $pK_a = 2.5$ of the radical cation and an assumed pK_a of 10 of the parent we calculate $E^\circ = 0.51$ V for the corresponding phenoxyl radical/phenolate couple. Then from eq 15 an apparent $\sigma^+_p = -0.84$ is calculated for the 4-HO–C_6H_4Te substituent. The electron-donating ability of the latter appears thus to lie between those of OCH_3 and OH.

Protonation/Hydration of Telluroxides. The above-mentioned protonation equilibrium (eq 9) of unsubstituted diphenyl telluroxide was also investigated with 4,4′-dihydroxy- and 4,4′-diamino-substituted diphenyl telluroxides. Their titration was conducted both spectrophotometrically and by electromotive force (emf) measurement:

$$(4\text{-HO–}C_6H_4)_2TeOH^+ + H_2O \rightleftharpoons (4\text{-HO–}C_6H_4)_2Te(OH)_2 + H^+ \qquad (16)$$

$$(4\text{-}H_2N\text{–}C_6H_4)_2TeOH^+ + H_2O \rightleftharpoons (4\text{-}H_2N\text{–}C_6H_4)_2Te(OH)_2 + H^+ \qquad (17)$$

The two equilibria turned out to be very close with $pK_a(16) = 5.75$ and $pK_a(17) = 5.85$. These values are but slightly higher than $pK_a(9) = 5.3$, the value for unsubstituted telluroxide. In a kinetic investigation[39] the transient presence of unhydrated neutral telluroxide was observed. The latter added water with a rate of ca. 10^3 s^{-1} to form the hydrate.

The nature of the hydration process was substantiated by adding small amounts of water to dry tetrahydrofuran containing $(4\text{-HO–}C_6H_4)_2TeO$ or $(4\text{-}H_2N\text{–}C_6H_4)_2TeO$. The smooth spectral changes eventually resulted in final spectra, which were essentially identical to those of $(4\text{-HO–}C_6H_4)_2Te(OH)_2$ or $(4\text{-}H_2N\text{–}C_6H_4)_2Te(OH)_2$ in water. From thermodynamic and kinetic considerations, we could also estimate K_{18} to be between 10 and 100:

$$Ar_2TeO + H_2O \rightleftharpoons Ar_2Te(OH)_2 \qquad (18)$$

This implies that unhydrated telluroxide is a stronger base than its corresponding hydrate, $Ar_2Te(OH)_2$, by 1.5 ± 0.5 pH units.

Two-Electron Reduction Potentials or the Telluroxide/Telluride, Sulfoxide/Sulfide, and Selenoxide/Selenide Couples in Water. Due to the poor water solubility of unsubstituted diphenyl chalcogenides, the following study was carried out with OH- or NH_2 substituted derivatives. By means of emf titration against pH we were able to determine the two-electron redox potentials of $(4\text{-HO–}C_6H_4)_2Te(OH)_2$ and $(4\text{-}H_2N\text{–}C_6H_4)_2Te(OH)_2$. Both couples yielded the same value, namely, 0.65 V vs NHE.

In the sense of the previous section E° of the corresponding unhydrated telluroxides should be higher by ca. $0.5 \times 0.06 \times \log(30) \approx 40$ mV, i.e., 0.69 V. Since these values appear to vary very little with the substituent, we believe the corresponding E° values for the unsubstituted analogue to be the same within a few tens of millivolts:

$$(C_6H_5)_2Te(OH)_2 + 2H^+ + 2e^- \rightleftharpoons (C_6H_5)_2Te + 2H_2O \qquad (19)$$

$$(C_6H_5)_2TeO + 2H^+ + 2e^- \rightleftharpoons (C_6H_5)_2Te + H_2O \qquad (20)$$

$$(C_6H_5)_2TeOH^+ + H^+ + 2e^- \rightleftharpoons (C_6H_5)_2Te + H_2O \qquad (21)$$

We thus set ${}^2E^0(19) = 0.65$ V, ${}^2E^0(20) = 0.69$ V, and ${}^2E^0(21) = 0.49$ V.

Although we have not measured the two-electron redox potential of diphenyl sulfoxide, this can safely be equated, within a few tens of millivolts, with that of DMSO. This conclusion can be drawn from the finding that in a 80/20% ethanol/water mixture the two-electron redox potentials of a number of dialkyl sulfoxides, diphenyl sulfoxide, and dibenzyl sulfoxide were found essentially identical.[40] Now, none of these values has ever been measured in pure water. However, from experimentally obtained thermodynamical data on dimethyl sulfide (DMS) and DMSO, Wood[41] could calculate ${}^2E^\circ(22)$ to be 0.574 V vs NHE. This value will also be assumed to hold for ${}^2E^\circ(23)$:

$$(CH_3)_2SO + 2H^+ + 2e^- \rightleftharpoons (CH_3)_2S + H_2O \qquad (22)$$

$$(C_6H_5)_2SO + 2H^+ + 2e^- \rightleftharpoons (C_6H_5)_2S + H_2O \qquad (23)$$

Finally, making the assumption that the redox potential of selenoxide is intermediate between those of sulfoxide and (unhydrated) telluroxide we tentatively set ${}^2E^\circ(24) = 0.63$ V:

$$(C_6H_5)_2SeO + 2H^+ + 2e^- \rightleftharpoons (C_6H_5)_2Se + H_2O \qquad (24)$$

Now, it is reasonable to assume that the difference in entropy and the free energy of solvation between diaryl chalcogenides and their corresponding oxides remain constant as one traverses the diaryl couples from S to Te. Therefore, the above two-electron redox potentials should yield the relative values of the dissociation energies of the chalcogen–oxygen double bonds in diaryl sulfoxides, selenoxides, and telluroxides. As can be seen, these decrease by ca. 3 kcal/mol from S=O to Se=O and from Se=O to Te=O. From the known[42,43] S=O dissociation enthalpy, 89.7 kcal/mol, in $(C_6H_5)_2S{=}O$ the strength of the Te=O bond in diaryl telluroxides is estimated to be 84 kcal/mol.

One-Electron Reduction Potentials of Sulfoxides, Selenoxides, and Telluroxides. In this work, one of the more interesting findings is the difference in reactivity of diaryl and dialkyl sulfoxides toward the hydrated electron (Table 1). Another notable observation was the inability of strongly reducing radicals such as $CO_2^{\bullet-}$ and the 2-hydroxy-2-methylethyl radical to reduce any oxide of diaryl chalcogenides except for the protonated species $(C_6H_5)_2TeOH^+$. To see whether these observations merely reflect thermodynamic properties or whether other parameters have to be invoked, we shall now estimate the one-electron reduction potentials of the oxides of diphenyl chalcogenides. Let us first consider $(C_6H_5)_2S{=}O$:

$$(C_6H_5)_2SO + e^- \rightleftharpoons (C_6H_5)_2SO^{\bullet-} \qquad (25)$$

$$(C_6H_5)_2SOH^\bullet \rightleftharpoons (C_6H_5)_2SO^{\bullet-} + H^+ \qquad (26)$$

$$(C_6H_5)_2S^{\bullet+} + H_2O \rightleftharpoons (C_6H_5)_2SOH^\bullet + H^+ \qquad (5)$$

$$(C_6H_5)_2S^{\bullet+} + e^- \rightleftharpoons (C_6H_5)_2S \qquad (27)$$

$$\overline{(C_6H_5)_2SO + 2H^+ + 2e^- \rightleftharpoons (C_6H_5)_2S + H_2O \qquad (23)}$$

Then we obtain:

$$E^\circ(25) = 2 \times {}^2E^\circ(23) - 0.059(\mathrm{p}K_a(26) + \mathrm{p}K_a(5)) - E^\circ(27)$$

We recall that at pH 14 at least 90% of $(C_6H_5)_2S^{\bullet+}$ was left, implying less than 10% hydrolysis.

Let us define

$$K_m = ([(C_6H_5)_2SOH^\bullet] + [(C_6H_5)_2SO^{\bullet-}])[H^+]/[(C_6H_5)_2S^{\bullet+}]$$

Then we have the relationship $K_m = K(5)(1 + K(26)/[H^+])$. At $[H^+] = K_m$ we get $K_m^2 = K(5)\ (K_m + K(26))$. If $K_m \ll K(26)$, then $K_m^2 = K(5)K(26)$ and if $K_m \gg K(26)$, $K_m = K(5)$.

However, it is always true that $K_m^2 \geq K(5)K(26)$ or $2\mathrm{p}K_m \leq \mathrm{p}K(5) + \mathrm{p}K(26)$. We saw that $\mathrm{p}K_m \geq 15$. Therefore, $\mathrm{p}K(5) + \mathrm{p}K(26) \geq 30$. Thus, we obtain $E^\circ(25) \leq 2 \times 0.57 - 0.59 \times 30 - 1.54 = -2.17$ V vs NHE. Clearly, this value is more negative than $E^\circ(CO_2^-/CO_2) = -1.90$ V,[44] which explains the unreactivity of the latter. On the other hand, since $\mathrm{p}K_a(26)$ is probably below 15, $E^\circ(25)$ is still much above −2.87 V, the E° of the hydrated electron.[45]

For comparison, let us now consider $E^\circ(\mathrm{DMSO/DMSO^{\bullet-}})$. From ref 1 it transpires that the corresponding $\mathrm{p}K_m$ for $\mathrm{DMS^{\bullet+}}$ is 10.2 ± 0.3:

$$\mathrm{DMS^{\bullet+}} + H_2O \rightleftharpoons \mathrm{DMS{-}OH^\bullet} + H^+ \qquad (28)$$

$$\mathrm{DMS{-}OH^\bullet} \rightleftharpoons \mathrm{DMS{-}O^{\bullet-}} + H^+ \qquad (29)$$

In a recent publication[8] the rate of expulsion of OH^- from DMS–OH• was reported to be $1.6 \times 10^6\ s^{-1}$. As the addition of OH^- to the $\mathrm{DMS^{\bullet+}}$ cation is most probably diffusion-controlled, i.e., ca. $10^{10}\ M^{-1}\ s^{-1}$, this implies that $\mathrm{p}K_a(28)$ is ca. 10, i.e., essentially equal to the experimental $\mathrm{p}K_m$. Consequently, $\mathrm{p}K_a(29)$ should be 10 or higher. We note that the $\mathrm{p}K_a$ of the diphenylketyl[46] radical is 9.2, while that of the 2-hydroxy-2-methylethyl[47] radical is as high as 12.2. This suggests that $\mathrm{p}K_a(29)$ is probably higher than $\mathrm{p}K_a(26)$ by about 3 units. Thus, we assume $\mathrm{p}K_a(29) \geq 14$. Insertion of these values into the above equation yields

$$E^\circ(\mathrm{DMSO/DMSO^{\bullet-}}) < -1.96 \text{ V vs NHE}$$

However, even assuming an improbably high $\mathrm{p}K_a(29)$ of 17, the reduction potential of DMSO would come out as −2.14 V, a value still more positive than the upper limit to $E^\circ(25)$. Thus, the low reactivity of DMSO and other dialkyl sulfoxides toward the hydrated electron cannot be explained thermochemically. It is tempting to suggest that the low reactivity of DMSO may be due to hydrate formation in water. However, this is contradicted by the fact that oxygen exchange takes place only under extreme conditions and rather slowly.[48]

DMSO is solvated though by water extremely strongly, presumably by way of a tight hydrogen bonding. Indeed, from thermodynamic data[36,41,42,43] we calculate the free energy of transfer of DMSO from gaseous to aqueous standard state to be ≈−9 kcal/mol, an exceptionally large negative value for a neutral species. However, the corresponding quantity for $(C_6H_5)_2SO$ can be estimated to be about the same. This follows from the fact that the S=O bond is stronger by about 2.5 kcal/mol in $(C_6H_5)_2SO$ as compared to DMSO, from the assumption of similar S=O bond dissociation entropies for the two compounds, from the very close values of the two-electron redox potentials and the estimated difference of 2 kcal/mol between the solvation free energies of $(CH_3)_23S$ and $(C_6H_5)_2S$, respectively (see above). Thus, the dilemma of the anomalous reactivity pattern of e_{aq}^- toward sulfoxides remains. In this context, it would be instructive to be able to compare the rates of electron attachment to dialkyl and diaryl sulfoxides in the gaseous phase or in nonpolar aprotic liquids.

Next, let us consider the two one-electron reduction equilibria:

$$(C_6H_5)_2TeOH^+ + e^- \rightleftharpoons (C_6H_5)_2TeOH^\bullet \qquad (30)$$

$$(C_6H_5)_2Te(OH)_2 + e^- \rightleftharpoons (C_6H_5)_2TeOH^\bullet + OH^- \qquad (31)$$

Utilizing ${}^2E^\circ(21) = 0.49$ V, $E^\circ((C_6H_5)_2Te^+/(C_6H_5)_2Te) = 1.14$ V and $\mathrm{p}K_a(8) = 10.3$ we obtain $E^\circ(30) = -0.77$ V. In equating $\mathrm{p}K_a(8)$ with the observed $\mathrm{p}K_m = 10.3$ we make the safe assumption that the pseudobase radical $(C_6H_5)_2TeOH$ deprotonates at a pH above 11, the lower limit to $\mathrm{p}K_a(26)$. $E^\circ(30)$ has, of course, such a high value that the facile reduction of protonated telluroxide by all reductants tested is readily accounted for. The reaction of the hydrated electron with telluroxide hydrate to yield the radical cation should be a dissociative electron transfer yielding OH^-. Consequently, the redox potential of process 31 should be considered. Insertion of the relevant values yields $E^\circ(31) = -1.28$ V. Thus, even though the process of dissociative electron transfer is kinetically somewhat impaired, the relatively high value of $E^\circ(31)$ provides an enormous driving force for the reaction with the hydrated electron and thus rationalizes the almost diffusion-controlled rate observed. However, not even a high driving force is sufficient to overcome the inertness of the telluroxide hydrate against $CO_2^{\bullet-}$.

As was mentioned earlier, the selenide radical cation might have a $\mathrm{p}K_a(7)$ as low as 13. Then, together with the other measured and estimated redox parameters, we calculate $E^\circ(32) \leq -1.65$ V vs NHE:

$$(C_6H_5)_2SeO + e^- \rightleftharpoons (C_6H_5)_2SeO^{\bullet-} \qquad (32)$$

This is an upper limit and given the uncertainties the true $E^\circ(32)$ could be lower by 100–200 mV. As $E^\circ(CO_2/CO_2^{\bullet-}) = -1.90$ V, the apparent reluctance of $CO_2^{\bullet-}$ to react with $(C_6H_5)_2SeO$ is not too surprising.

Chalcogen–Oxygen Single-Bond Strengths in the OH Adducts to the Chalcogenides. In a previous section it was concluded that the strength of the chalcogen–oxygen double bonds in sulfoxides, selenoxides, and telluroxides decreased by about 6 kcal/mol upon going from sulfoxide to telluroxide. It would be interesting to investigate the trend with the corresponding chalcogen–oxygen single bonds. We shall then estimate the free energies of dissociation of reactions 33–35. From $K(5)$, $K(7)$, and $K(8)$ and

$$(C_6H_5)_2S\text{–}OH^\bullet \rightleftharpoons (C_6H_5)_2S + OH^\bullet \tag{33}$$

$$(C_6H_5)_2Se\text{–}OH^\bullet \rightleftharpoons (C_6H_5)_2Se + OH^\bullet \tag{34}$$

$$(C_6H_5)_2Te\text{–}OH^\bullet \rightleftharpoons (C_6H_5)_2Te + OH^\bullet \tag{35}$$

by use of the determined one-electron reduction potentials of the radical cations as well as that of the $OH^\bullet$ radical,[28] we calculate $\Delta G^\circ(33) \leq 7$ kcal/mol, $\Delta G^\circ(34) \leq 14$ kcal/mol and $\Delta G^\circ(35) = 22$ kcal/mol. For example, the formula for $\Delta G^\circ(33)$ is as follows:

$$\Delta G^\circ(33) = 1.364 \log(K_5) + 23.06\{E^\circ(OH^\bullet, H^+/H_2O) - E^\circ(Ph_2S^{\bullet+}/Ph_2S)\}$$

Clearly, the stability of the chalcogen–oxygen single bonds in these adducts shows a reverse trend to the one observed for the corresponding double bonds.

To conclude these calculations, we shall derive the S–O single-bond strength in the DMS–OH adduct. We already know that $pK_a(28) = 10.2$.

Then we obtain $\Delta G^\circ(36) = 10$ kcal/mol, which is close to but still higher by at least 3 kcal/mol than $\Delta G^\circ(33)$:

$$DMS\text{–}OH \rightleftharpoons DMS + OH^\bullet \tag{36}$$

Another interesting question is how a substituent on a certain diaryl chalcogenide would affect the chalcogen–oxygen single bond in the OH adduct. First, we recall that the two-electron redox potentials and protonation equilibria of OH- and NH_2-substituted diaryl telluroxides were identical, which implies that the Te═O double-bond strength in telluroxide is substituent independent. We also found above that the pK_a values of pseudobase formation of unsubstituted and NH_2-substituted diaryl telluride radical cations were about the same, although their one-electron reduction potentials differed by as much as 0.34 V. This implies that the NH_2 substituent stabilizes the OH adduct against homolysis by ca. 0.34 eV.

In conclusion, the resistance against homolysis of a chalcogen–oxygen bond in the OH adduct will be the stronger the lower the ionization potential of the substituted chalcogenide. This shows that a three-electron bond to O is stabilized by the inflow of extra electrons. In a symmetrical way it was found[7] that, with respect to homolysis, the three-electron bond to dimethyl sulfide was the stronger the higher the electron affinity of the halogen atom attached,[7] i.e., the DMS–Cl adduct was the strongest, the I adduct the weakest, with the Br adduct in between. Not unexpectedly, however, the heterolytic bond strengths of the halogen adducts displayed a reverse order.

Production of $(C_6H_5)_2S^{\bullet+}$ in Water–Alcohol Mixtures. Due to solubility problems, it is sometimes desirable to study the oxidation of substrates in other solvents than water. Unfortunately, the radical cations, formed upon irradiation of organic solvents, transform into nonoxidative carbon centered radicals through deprotonation. The usual remedy has been to generate[49] halogenated methylperoxyl radicals through dissociative electron attachment to halomethanes in the presence of O_2. However, these radicals are not exclusively one-electron oxidants, as they are also capable of reacting by way of oxygen atom transfer.[50,51] We have found that $(C_6H_5)_2S^{\bullet+}$ is produced with a yield of 1.7×10^{-7} M/J when an argon purged solution of $(C_6H_5)_2SO$ (10^{-3} M) in 1/1 vol mixtures of water and 2-methyl-2-propanol is pulse irradiated. Although the yield of this oxidative radical is significantly lower than in water, it has the advantage of only reacting via one-electron oxidation with a substantial potential.

Experimental Section

Pulse radiolysis was performed at room temperature utilizing doses of 2–15 Gy/pulse corresponding to 1.2×10^{-6}–9×10^{-6} M of radicals. The 7-MeV microtron accelerator[52] and the computerized optical detection system[53] have been described elsewhere. Dosimetry was performed by means of an aerated 10^{-2} M KSCN solution taking[54] $G\epsilon = 2.23 \times 10^4$ 100 eV^{-1} M^{-1} cm^{-1}. The solutions were made up in Millipore-deionized water. The two-electron redox potentials of telluroxide/telluride couples were measured with a platinum electrode against SCE, the calomel reference having been calibrated against the quinhydrone electrode. All values are given versus NHE. Melting points (uncorrected) were determined by using a Büchi 510 melting point apparatus. ^1H NMR spectra were obtained with a Bruker AC-F 250 instrument operating at 250 MHz and recorded for $CDCl_3$ solutions containing tetramethylsilane as the internal standard. Elemental analyses were performed by Analytical Laboratories, Engelskirchen, Germany.

Chemicals: 2-Methyl-2-propanol (Merck p.a.), 2-propanol (Aldrich HPLC grade), NaN_3 (Aldrich 99%), NaBr (Aldrich 99%), HCO_2Na (Aldrich 99%+), NaOH (Aldrich 99.99%), H_2SO_4 (Merck suprapure), $NaB_4O_7 \cdot 10H_2O$, KH_2PO_4, and K_2HPO_4 (Merck p.a.), diphenyl sulfide (Aldrich 98%), dibutyl sulfoxide (Aldrich 96%), diphenyl selenide (Eastman Kodak), and bis(4-hydroxyphenyl) sulfide (Crown Zellerbach Corp.) were used as received. Diphenyl sulfoxide (Aldrich 97%) was recrystallized from CH_2Cl_2/hexanes before use. Diphenyl selenoxide,[55] biphenyl telluride,[56] diphenyl telluroxide,[57] bis(4-aminophenyl)sulfide,[58] bis(4-aminophenyl) selenide,[59] bis(4-aminophenyl) telluride,[60] bis(4-aminophenyl) telluroxide,[39] bis(4-hydroxyphenyl) telluride,[22] bis(4-hydroxyphenyl) telluroxide,[39] and bis (*tert*-butyl) sulfoxide[61] were prepared according to literature procedures.

Bis(4-hydroxyphenyl) sulfoxide: To a stirred solution of bis(4-hydroxyphenyl) sulfide (1.0 g, 4.6 mmol) in a mixture of MeOH (1.5 mL) and CH_2Cl_2 (18 mL) was added dropwise *m*-chloroperoxybenzoic acid (1.0 g 85%, 4.9 mmol) in CH_2Cl_2 (10 mL). After 1 h, the while crystalline material formed (1.02 g, 95%) was filtered and recrystallized from $MeOH/CH_2Cl_2$/hexanes, mp 201 °C (lit.[62] 201 °C).

Bis[4-(carboxymethoxy)phenyl] sulfide: To a stirred solution of bis(4-hydroxyphenyl) sulfide (3.0 g, 13.8 mmol) in dry dimethyl sulfoxide (40 mL) under argon was added NaH (0.90 g, 80%, 30.0 mmol) in portions (gas evolution). Methyl bromoacetate (5.0 g, 32.7 mmol) was then added and the temperature kept at 90 °C for 4 h. The cooled reaction mixture was poured into water and extracted with CH_2Cl_2. Chromatography (SiO_2/CH_2Cl_2) afforded 3.08 g (62%) of bis[4-(carbomethoxymethoxy)-phenyl sulfide, ^1H NMR δ 3.73 (s, 6 H), 4.54 (s, 4 H), 6.76 (d, 4 H), 7.19 (d, 4 H). To a stirred solution of bis[4-(carbomethoxymethoxy)phenyl sulfide (0.50 g, 1.38 mmol) in THF (30 mL) was added $LiOH \cdot H_2O$ (0.29 g, 6.90 mmol) in water (20 mL). The reaction mixture was then kept for 19 h at ambient temperature, poured into water, acidified and extracted with CH_2Cl_2. The crystalline material obtained after drying and evaporation of the organic phase was recrystallized from $EtOH/H_2O$ to give 0.44 g (96%) of the title compound, mp 203–05 °C. Anal. Calcd for $C_{16}H_{14}O_6S$: C, 57.48; H, 4.22. Found: C, 57.33; H, 4.31. ^1H NMR δ ($CDCl_3$/DMSO-d_6 = 9/1) 4.57 (s, 4 H), 6.85 (d, 4 H), 7.25 (d, 4 H).

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