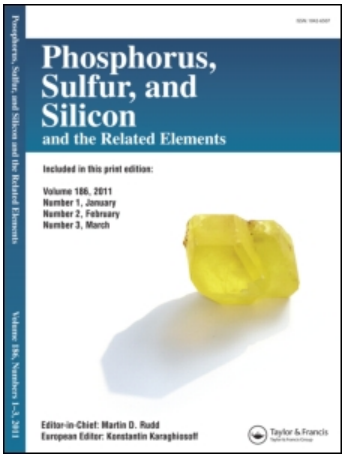

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FREE RADICAL AND ELECTROCHEMICALLY INDUCED OXIDATION OF ORGANIC SULFUR-, SELENIUM- AND PHOSPHORUS-COMPOUNDS

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A series of $MeS(CH_2)_nSMe$, $MeS(CH_2)_nSeMe$, $MeSe(CH_2)_nSeMe$ (with n = 1-5), and $RS(CH_2)_nPEt_2$ (n = 2-4) have been investigated with respect to their radiation chemical one-electron and electrochemical two-electron oxidations. The results essentially confirm an interaction of the two respective heteroatoms in these compounds already in the unoxidized state. Oxidation is thus achieved by removal of antibonding σ* electrons.

Key Words 1,ω-bis-(methylthio)alkanes, 1-(methylthio)-ω-(methylseleno)alkanes, 1,ω-bis-(methylseleno)alkanes, 1-(alkylthio)-ω-(diethylphosphino)alkanes, one-electron oxidation, two-electron oxidation, radical cations, three-electron bonds, sulfoxide formation, pulse radiolysis, cyclic voltammetry, mass spectroscopy.

INTRODUCTION

In earlier studies on the oxidation of simple thioethers and various open chain and cyclic dithia compounds the transient formation of sulfur-centered radical cations has been established.[1] Particularly stable radical cations result from interaction of the unpaired p-electron from the oxidized sulfur with a free p-electron pair from a second sulfur, a process which can be achieved both *intra-* as well as *inter*molecularly. The new sulfur-sulfur bond established thereby contains a total of three electrons, two of which being bonding (σ) and the third antibonding (σ*) in nature. Such $(>S\therefore S<)^+$ species generally exhibit lifetimes up to milliseconds and can conveniently be studied by time-resolved optical absorption spectroscopy, e.g. the radiation chemical technique of pulse radiolysis, because of their pronounced absorption band in the near UV and visible range.[1] In principle, such two-center-three-electron bonds can be established between any two hetero atoms. Several examples on $(>S\therefore S<)^+$ analogues where one of the sulfurs has been substituted by oxygen,[2] nitrogen,[3] phosphorus,[4] and halogens (Cl, Br, I)[5] have been reported.

Electrochemical studies with several organic dithia and other functionalized sulfur compounds have indicated that their oxidation could benefit significantly from neighboring group effects, particularly "lone pair- lone pair" interaction.[6,7] The electrochemical

oxidation of organic sulfides under the experimental conditions used generally leads to the two-electron product sulfoxide (although seemingly only in the presence of at least some water). In this respect the electrochemical systems differ significantly from the free radical induced oxidations which usually constitute one-electron processes. Nevertheless, certain correlations become apparent between the two methods with respect to the peak potentials at which electrochemical oxidation takes place and some properties of the transient three-electron bonded one-electron oxidation species.[1,8,9]

In our present study we now want to focus on the following aspects: (i) To substantiate the correlation between the peak potential for the electrochemical oxidation of a series of 1,ω-bis-(methylthio)alkanes and the optical characteristics of the *intra*molecular $(>S\therefore S<)^+$ radical cations generated in the $^{\bullet}OH$ radical induced oxidation of these compounds. (ii) To extend these studies to 1-(methylthio),ω-(methylseleno)alkanes and 1,ω-bis-(methylseleno)alkanes, i.e., compounds where the sulfur atoms have successively been exchanged by selenium. (iii) To study the corresponding dependencies and characteristics for a series of 1-(alkylthio),ω-(diethylphosphino)alkanes, particularly in view of a varying alkyl substituent at sulfur.

EXPERIMENTAL

All compounds investigated have been synthesized according to procedures described in principle in the literature[10,11] and analyzed for their identity and purity by conventional NMR and GC-MS methods. In case of the phosphine compounds particular care had to be taken to avoid oxygen both during the synthetic procedure and the experiments with these compounds.

Electrochemical CV studies were generally carried out with $2x10^{-3}$ M solutions of the compound of interest in acetonitrile with 0.1N tetraethylammonium perchlorate (TEAP) as supporting electrolyte. The reference electrode was Ag/0.1 N $AgNO_3$/0.1 N TEAP in acetonitrile The electrochemical unit comprised a Princeton Applied Research 273A potentiometer, a 286 AT computer with a Princeton Applied Research model 270 electrochemical analysis software 3.0, and a rotating disk electrode Methrom 628-10 with a Pt or glassy carbon electrode tip. The scan rate was varied between 25 and 500 mV s^{-1}. If not specifically noted the experiments were conducted at 250 mV/s.

The pulse radiolysis experiments were carried out with aqueous solutions of typically 10^{-4} M solute concentration which were deoxygenated by saturation with N_2O. In such solutions 90% of the reactive species formed upon irradiation are $^{\bullet}OH$ radicals which initiate the one-electron oxidation processes. (The remainder are $H^{\bullet}$ atoms which do not oxidize the heteroatom compounds). The technique of pulse radiolysis, the detection of transient absorptions and analysis of data have been described in detail elsewhere.[12]

All experiments have been carried out at room temperature. The experimental error limit was estimated to ±5 nm for the optical measurements (λ_{max}), and ±0.05 V for the determination of the electrochemical peak potentials.

RESULTS AND DISCUSSION

1,ω-bis(Methylthio)alkanes

A cyclic voltammogram showing the oxidation of $MeS(CH_2)_3SMe$ is displayed in Fig. 1. It shows three oxidation peaks at 0.74 V, 1.45 V, and 2.18 V. The respective peak potentials for several other 1,ω-bis(methylthio)alkanes and simple thioethers are listed in Table I. (All potentials are measured against Ag/0.1N $AgNO_3$ as reference. Addition of 0.337 V or 0.580 V yields the corresponding data against SCE or NHE, respectively).

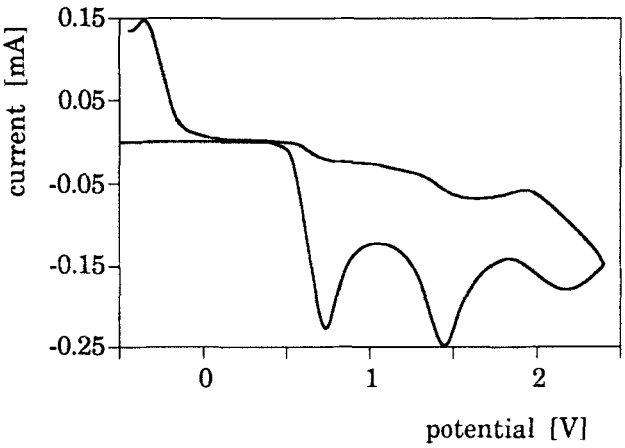


FIGURE 1 Cyclic voltammogram of a $2x10^{-3}$ M solution of $MeS(CH_2)_3SMe$ in acetonitrile with 0.1 N TEAP measured against Ag/$AgNO_3$ (0.1N). Scan rate: 250 mV/s; Pt-electrode

TABLE I Oxidation peak potentials for $MeS(CH_2)_nSMe$ (n = 1-4), and λ_{max} for the respective *intra*molecular radical cations formed upon one-electron oxidation of these compounds (n = 1-5).

compound	1. peak	2. peak	3. peak	λ_{max} $(S\therefore S)^{+}$ [13]
R–S–R	1.450 (±0.040) V			
S – 1 – S	1.130 V	1.910 V		660 nm
S – 2 – S	1.095 V	1.640 V	2.190 V	525 nm
S – 3 – S	0.742 V	1.450 V	2.180 V	440 nm
S – 4 – S	0.900 V	1.400 V	2.200 V	460 nm
S – 5 – S				475 nm

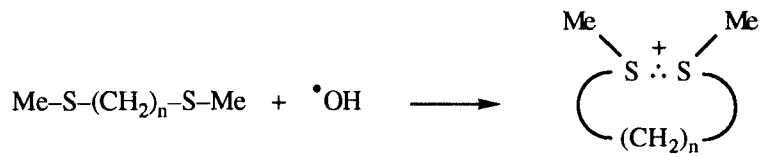
The first oxidation peak potential for the oxidation of all dithia compounds is generally lower than that for the oxidation of simple aliphatic monosulfides (thioethers). Further-

more, it assumes a minimum value at n=3, i.e., for the compound with three methylene groups between the two sulfurs. This latter finding is not true anymore for the second oxidation where the potentials seem to level off at a lower value of about 1.4 V with increasing n. A practically constant value is finally obtained for the third potential. In case of n=1 only two waves are observed.

At least the first two oxidations exhibit practically no reductions and are therefore considered to be irreversible. This holds irrespective of the scan rate which was varied from 25-500 mV/s. The number of electrons, n_e, involved in the oxidation process was evaluated via the Randles-Sevcik equation[14] which relates the measured peak current with the square root of the scan rate. Assuming a diffusion coefficient of the sulfides of 10^{-5} cm^2/s $n_e \approx 1.9$ is obtained indicating a two-electron process. This finding is in agreement with other studies on the electrochemical oxidation of organic sulfides.[9] A reasonable rationale would then be that the first step proceeds via a disulfide dication which subsequently irreversibly converts into the sulfoxide.

$$2\ -S- \xrightarrow{-2e^-} (>S-S<)^{2+} \rightarrow >S{=}O + -S- + 2\,H^+ \qquad (1)$$

An interesting correlation exists between the electrochemical data for the first two-electron oxidation step and the optical characteristics of the *intra*molecular radical cations, which are formed in the one-electron oxidation of the dithia compounds. The latter are generated, for example, upon pulse radiolysis of an N_2O saturated aqueous solution of $MeS(CH_2)_nSMe$ by reaction with the oxidizing hydroxyl radical.[1,13]



(2)

The respective λ_{max} of these radical cations also show an extreme value at n=3 as can be appreciated from the values listed in Table I. It is well established that this reflects the particular stability of the, in this case, five-membered ring structure involving the three methylene carbons and the two sulfurs linked together by the $2\sigma/1\sigma^*$ three-electron bond.[1]

Theoretical calculations[15] have shown that the optical transition takes place between the upper most doubly occupied energy level, which represents a σ-orbital affected by the nonbonding electrons, the nature of the substituents and structural parameters, and the singly occupied σ* orbital. Schematically this is depicted in Figure 2. The most favorable p-orbital overlap for the compound with n=3 results in a maximum σ/σ^* separation and thus most blue-shifted absorption. For n=1 the orbital interaction is less favorable and accordingly the σ/σ^* separation and the optical transition energy becomes smaller.

The electrochemical findings can easily be rationalized by the same considerations assuming a lone pair - lone pair interaction in the unoxidized molecules and creation of the associated σ and σ* orbitals. Both energy levels are doubly occupied, as depicted in Figure 3, and the electron to be removed in the first oxidation step would be an antibonding one. Considering the compounds with different number of methylene carbons the

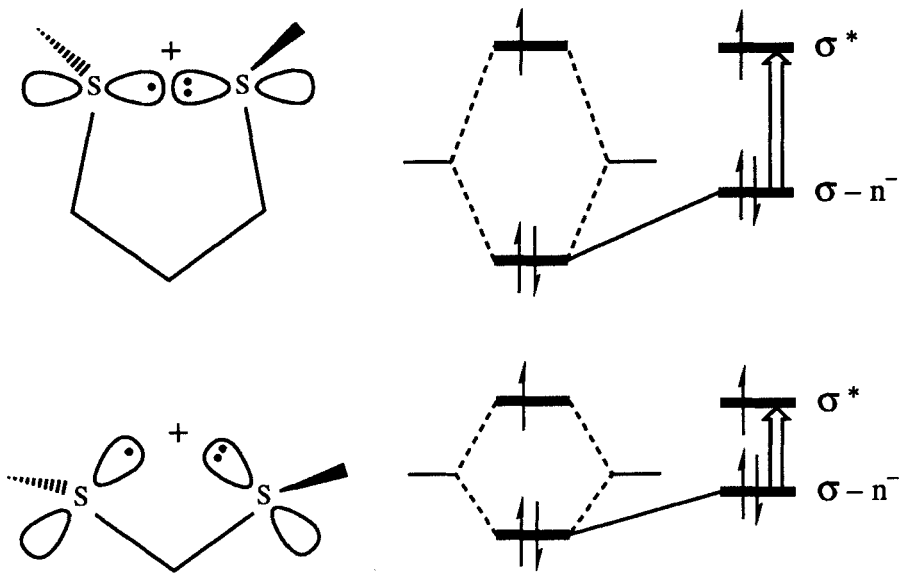


FIGURE 2 Orbital overlap and MO energy levels for dithia compounds with n=1 and 3

strongest orbital interaction, i.e., the largest σ/σ* splitting, is expected for the compound with n=3 while the σ/σ* energy difference becomes smaller for all others. This is illustrated schematically in Figure 3 for two examples.

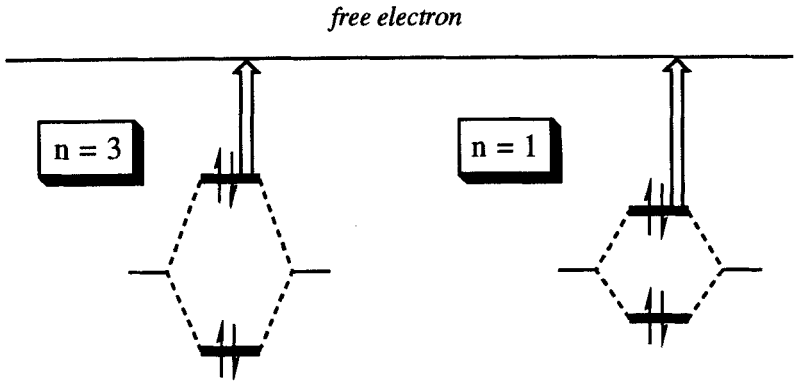
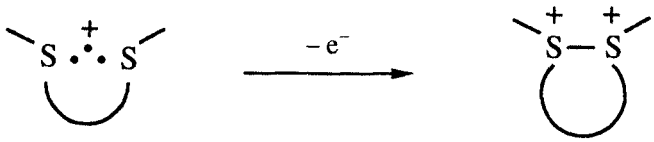


FIGURE 3 Relative energies required for removal of electrons considering "lone pair - lone pair" interaction

Since the electrons to be removed upon oxidation are those located in the σ* energy level it would accordingly take the least energy for the n=3 compound while a higher energy is required, for example, for the n=1 system. Lone pair - lone pair interaction thus provides one rationale for the trend in the peak potentials for the first oxidation step.

Alternatively (or additionally) the common trend in electrochemical and optical data could reflect the thermodynamic stability of the respective three-electron intermediate radical cations.

That the second ionization of a dithia compound does indeed involve an antibonding electron and has also been demonstrated by mass spectrometry experiments on the collision-induced oxidation of the mass-selected three-electron bonded radical cation.[16]



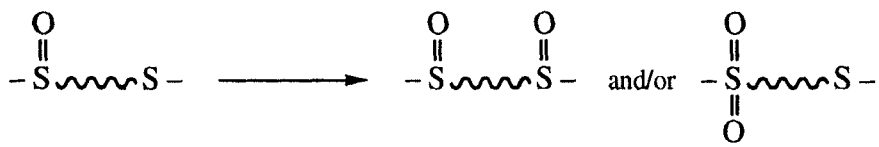
(3)

In the series of the *intra*molecular radical cations with the largest σ/σ^* splitting and therefore highest σ^* energy level is obtained, as mentioned above, that for n=3. Lower values pertain to the S∴S bonded species derived from the compound with n=4 and n=2 as reflected in the energies for the optical transitions of 440 nm, 460 nm, and 525 nm (Table I). In view of our considerations the $(>S\therefore S<)^+$ ionization energies should be lowest for the n=3 system and increase over n=4 to n=2. This is indeed the case as proven by the experimental values of 12.3 eV, 12.7 eV, and 13.3 eV, respectively.

In summary, the results presented and discussed so far thus provide ample evidence for an appreciable sulfur-sulfur interaction already in the unoxidized dithia compounds. Furthermore it is possible to rationalize both the two-electron oxidation process observed in electrochemistry as well as the properties of the one-electron oxidation intermediate on the basis of the same concept, namely, the presence of antibonding σ^* electrons.

Let us now return to the electrochemical data and briefly discuss the second and third oxidation wave observable in the cyclic voltammograms. It can reasonably be assumed that the two-electron oxidation product of the first oxidation step is, at least for the compounds with n≥2, the respective sulfoxide. The water necessary to react with the dication seems to be present as trace impurity in the acetonitrile. The difficulty to remove residual water from this solvent is well known.

The second oxidation wave could then be attributed to either processes which lead to either the disulfoxide or the sulfone, or both products. From the electrochemical data it is not possible to distinguish between the two possibilities.

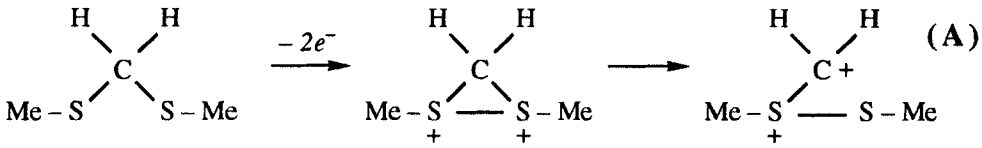


(4)

It is noted that the peak potentials of the second step approach the value measured for oxidation of the isolated sulfide function (1.45 V) the further the sulfide function becomes separated from the sulfoxide function. On the other hand, the isolated sulfoxide-to-sulfone oxidation takes place at 1.55-1.60 V, i.e., at potentials not too different from the sulfide oxidation. The somewhat higher peak potential for the n=2, and particularly the 1.91 V

value for the n=1 compound may be interpreted in terms of some electron withdrawing from the yet to be oxidized sulfide function by the neighboring sulfoxide function. This potential may be raised sufficiently positive so that the sulfoxide-to-sulfone oxidation becomes more favorable.

The third oxidation wave, showing no dependence on the molecular structure at all, peaks at about 2.2 V. An unambiguous assignment is not possible without product identification, preferably from controlled potential experiments. In addition, other products than sulfoxides have to be taken into consideration. It is well established,[17-19] for example, that oxidation of the n=1 compound results in sulfur-carbon bond cleavage. In the presence of water as nucleophile our particular n=1 compound would lead to dimethyl disulfide and formaldehyde:



$$(A) + H_2O \longrightarrow MeSSMe + HCHO + 2H^+ \qquad (5)$$

Oxidation of these products take, however, place at lower potentials than that of the second electrochemical peak and they are, therefore not likely to account for the 1.91 V oxidation wave.

1-(Methylthio)-ω-(methylseleno)alkanes

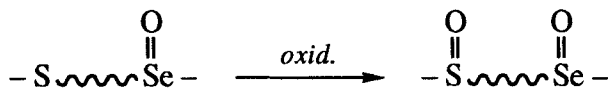
Very similar results, from the qualitative point of view, have been obtained if one of the sulfur atoms in the dithia compounds is substituted by selenium. Both the peak potentials for the first two-electron oxidation and the optical transition of the one-electron oxidation intermediate, the S∴Se three-electron bonded radical cation, exhibit the lowest values for the n=3 compound. The actual data are summarized in Table II.

TABLE II Oxidation peak potentials for $MeS(CH_2)_nSeMe$ (n = 1-5), and λ_{max} for the respective *intra*molecular radical cations formed upon one-electron oxidation of these compounds (n = 1-5).

compound	1. peak	2. peak	3. peak	λ_{max} $(S\therefore Se)^+$
S – 1 – Se	0.894 V	1.520 V	2.00 V	620 nm
S – 2 – Se	0.850 V	1.610 V	2.24 V	550 nm
S – 3 – Se	0.600 V	1.625 V	2.23 V	435 nm
S – 4 – Se	0.665 V	1.410 V	2.10 V	455 nm
S – 5 – Se	0.791 V	1.410 V	2.03 V	470 nm

From the quantitative point of view, the λ_{max} values do not differ significantly from those for the entirely sulfur-centered species. The first oxidation peak potentials are, however, lower by about 0.2 V by comparison, reflecting the lower electronegativity of the selenium atom.

It is interesting to note that the second oxidation peak assumes the same number, 1.41 V, as for the –S–n–S– compounds at higher n. This would be compatible with the first oxidation step to yield the selenoxide and the second step referring to the oxidation of the remaining sulfide function:



(B) (6)

The third oxidation step may then be due to the further oxidation of **(B)**. Clearly the 5-membered ring configuration which so favorably lowered the oxidation peak potential for the first step does not exert a similar effect for the second and third peak. The latter appear, in fact, even slightly higher for the –S–3–Se– compound indicating an adverse, i.e., potential-raising effect. As these differences are relatively small they should, however, not be overinterpreted.

1,ω-bis(Methylseleno)alkanes

The diseleno compounds show a very similar picture with respect to the first oxidation peak potential and the trends in λ_{max}. The respective data being summarized in Table III.

TABLE III First oxidation peak potentials for $MeSe(CH_2)_nSeMe$ (n = 1-5) and R_2Se, and λ_{max} for the respective *intra*molecular radical cations formed from the diseleno compounds upon one-electron oxidation.

compound	1. peak	λ_{max} $(Se.\therefore Se)^+$
R – Se – R	0.97 V	
Se – 1 – Se	0.820 V	680 nm
Se – 2 – Se	0.600 V	550 nm
Se – 3 – Se	0.500 V	440 nm
Se – 4 – Se	0.580 V	460 nm
Se – 5 – Se	0.660 V	470 nm

The minimum peak potential for the n=3 compound is further lowered by introducing the second selenium by comparison with the sulfur-selenium compound. Relative to the simple aliphatic selenides, R_2Se (e.g. Me–Se–*n*-Bu), the decrease amounts, however, only to 0.47 V while the corresponding decrease amounted to 0.69 V in going from R_2S to –S–3–S–. This probably reflects the lower ionization energy of the selenium atom relative to sulfur in the simple chalcogenide rather than a weaker orbital interaction in the diselenide.

The relative orbital energy differences seem to be very similar again to the sulfur containing compounds as indicated by the practically identical λ_{max} values for the optical transitions.

Certain other feature are, however, very different for the diseleno compounds. For example, only two oxidation waves were observed for the compounds with n=3 and 4, the second at about 1.9 V. For the compounds with n=5 an additional oxidation is apparent at about 1.1 V, and for n=1 and 2 a total of four waves have been observed with the second $E_{p,ox}$ at 1.0 and 0.85 V, respectively, and the third $E_{p,ox}$ at about 1.7 V irrespective of n. Again, and in analogy with the sulfides, it seems reasonable to attribute the secondary oxidations to selenoxides and selenones. However, the possibility of selenium-carbon bond breakage presumably opens further routes to other products, including inorganic selenium ions and oxides. At this stage any interpretation would thus be unjustifiably speculative.

Another characteristic difference with the sulfur compounds is the appearance of a reduction wave with increasing scan rate. This is shown in Figure 4 for one particular diseleno compound.

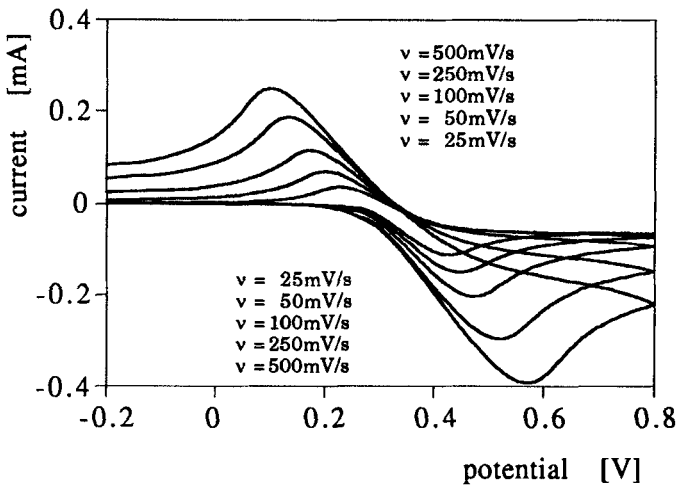
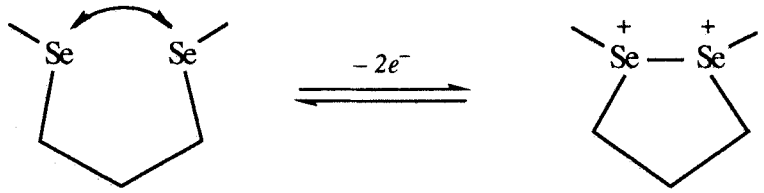


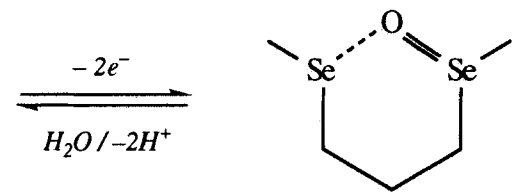
FIGURE 4 CV's obtained from solutions of $2x10^{-3}$ M Me–Se–$(CH_2)_3$–Se–Me in acetonitrile containing 0.1N TEAP, measured against Ag / 0.1N $AgNO_3$ and with a Pt-electrode at various scan rates.

In fact, with increasing scan rate the overall picture assumes more and more that of an irreversible process. It must be recognized though that the peak potentials for oxidation and reduction are separated by quite a significant potential difference, namely 0.40 V at a scan rate of 50 mV/s. Furthermore, this difference increases with the scan rate and attains a value of 0.72 V at 500 mV/s. Therefore, it cannot be a clean reversible electron transfer through the electrode's double layer, and overpotential as well as specific ad- or desorption phenomena may have to be forwarded for a quantitative interpretation of the results.

Chemically, the increasingly pronounced reduction wave and quasi-reversibility could be explained by a diseleno-dication or perhaps an easily reducible bridged oxide as depicted in the following structures.



(7)



(8)

If this is true it would point to a longer lifetime of the diseleno-dication with respect to the subsequent selenoxide formation as compared to the corresponding sulfur species. Conventional chemistry on the oxidation of organic chalcogenides seem in support of this conclusion.[20]

It is interesting to note that the appearance of reduction waves with increasing scan rates, i.e., possible reversibility, is also indicated for 1-(methylthio),ω-(methylseleno)-alkanes. This clearly identifies the selenium atom to be responsible for the observed effects.

1-(Alkylthio)-ω-(diethylphosphino)alkanes

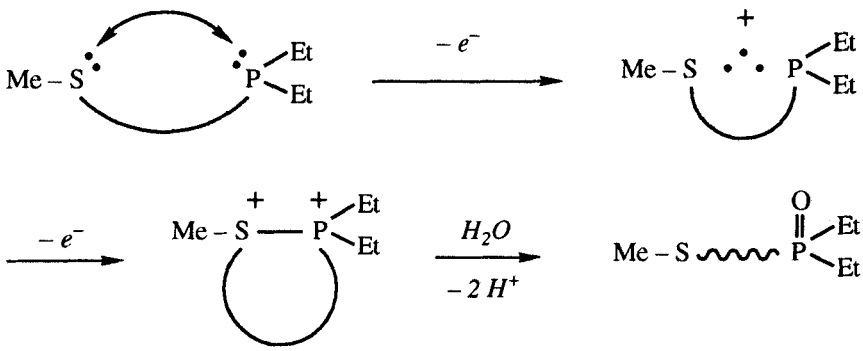
Introduction of a phosphorus atom into a sulfur containing chain creates the possibility for an S–P interaction. This has been demonstrated with respect to the formation of an *intra*molecular $(-S\therefore P<)^+$ radical cation upon $^{\bullet}OH$-induced oxidation of 1-(methylthio)-3-(diethylphosphino)propane, i.e., the compound with n=3.[4] We now extended our earlier studies by investigation a series of such compounds with different chain lengths and alkyl substituents. As can be seen from the data listed in Table IV the n=3 compound is, as expected, favored with respect to both, the stability of the radical cation (reflected in λ_{max}) and the relative ease to be oxidized electrochemically (first $E_{p,ox}$). Qualitatively the 1-(alkylthio)-ω-(diethylphosphino)alkanes thus follow suit with all the other sulfur and selenium compounds discussed so far. They clearly indicate again a reasonably strong interaction of the two heteroatoms already in the unoxidized molecule.

On an absolute basis the first $E_{p,ox}$ is even lower than that for the diselenium compound. This can best be rationalized by a lower ionization potential of the phosphorus compared with the two chalcogenides. The presence of phosphorus also exerts a noticeable influence on the optical transition energy for the radical cations. Compared with all the other sulfur and selenium species the respective λ_{max} are significantly blue-shifted. Possibly, this may be associated with the molecular orbital involved in the three-electron bonds. While for the sulfur- and selenium-centered species only p-orbitals participate, the interacting orbital of phosphorus is likely to be a hybrid with significant s-orbital contribution.

TABLE IV First and second oxidation peak potentials for $MeS(CH_2)_nPEt_2$ (n = 2-4), and λ_{max} for the respective *intra*molecular radical cations upon one-electron oxidation by $^{\bullet}OH$ radicals. [a] only in absence of acid; [b] addition of $HClO_4$

compound	1. peak [a]	λ_{max} $(S\therefore P)^+$	2. peak
S – 2 – P	0.462 V	480 nm	1.60[a]; 158[b]
S – 3 – P	0.370 V	385 nm	1.46[a]; 145[b]
S – 4 – P	0.467 V	440 nm	1.47[a]; 145[b]

The oxidation mechanism, split into two consecutive one-electron steps, is formulated in reaction sequence:



(9)

(9a)

In the electrochemical process both electrons are removed at once, and there is no indication of any reversibility.

The second electrochemical oxidation wave peaks at potentials which reminiscent of the disulfur and sulfur-selenium systems. At larger sulfur-phosphorus separation the $E_{p,ox}$ approach the value measured for the oxidation of an isolated sulfoxide group. It is therefore concluded that the first oxidation occurs at the phosphorus, leading to the formation of the respective phosphinoxides.

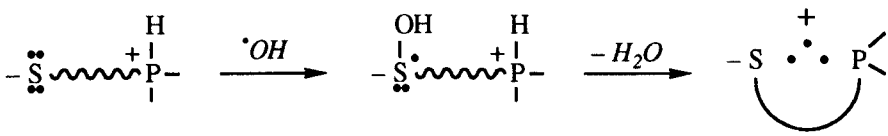
One important additional aspect needs to be considered for the phosphines, namely, the relative ease of their possible protonation to the respective phosphonium salts. The first step of the electrochemical oxidation thus occurs only with the deprotonated phosphine. When $HClO_4$ is added (slightly in excess to the 1-(alkylthio)-ω-(diethylphosphino)alkanes and the phosphorus becomes protonated phosphonium the first, low potential oxidation does not occur anymore.

$$-S\text{----(n)----}P< \quad + \quad H^+ \quad \rightleftarrows \quad -S\text{----(n)----}P(H)^+< \qquad (10)$$

The second oxidation wave remains, however, at practically the same potential as for the deprotonated compound. These findings fully support our above conclusion that phos-

phorus is the primary target for oxidation and the 1.45 V wave refers to the oxidation of the sulfide function.

In aqueous solution pK measurements gave values of about 6.5 for equilibrium 10. An interesting special mechanism applies to the hydroxyl radical induced process where oxidation to the $(-S\therefore P<)^+$ radical cation occurs in moderately acid solutions (pH ≥ 3). It involves an $^{\bullet}OH$-adduct at sulfur.



(11)

By loss of water, or more precisely by loss of a hydroxyl ion plus the phosphonium proton, the transient hydroxyl adduct converts into the three-electron bonded radical cation. At very low pH external protons successfully take over and only an *inter*-molecular, purely sulfur-centered radical cation can be formed under participation of a second unoxidized molecule. (The phosphorus does not play any active role in this case).

$$-S^{\bullet}(OH)\text{-----} + H^+ + -S\text{-----} \rightarrow (>S\therefore S<)^+ + H_2O \qquad (12)$$

In basic solutions the driving force for the S–P interaction is much higher because of the free electron pair at phosphorus. In fact, the absorption of the $(-S\therefore P<)^+$ grows in immediately with the $^{\bullet}OH$ reaction while there is a delay in acid systems indicating a lifetime of a few μs for the protonated phosphonium intermediate. Corresponding absorption-time traces are shown in Figure 5.

The results are corroborated by time-resolved conductivity measurements. Thus the formation of the radical cation plus the hydroxide ion in basic solution is accompanied by a corresponding increase in conductivity. In acid solution, on the other hand, no overall change in conductivity is expected, and accordingly not found, as can be deduced from equation 11. (The conversion of one cation into another causes at most only minimal changes).

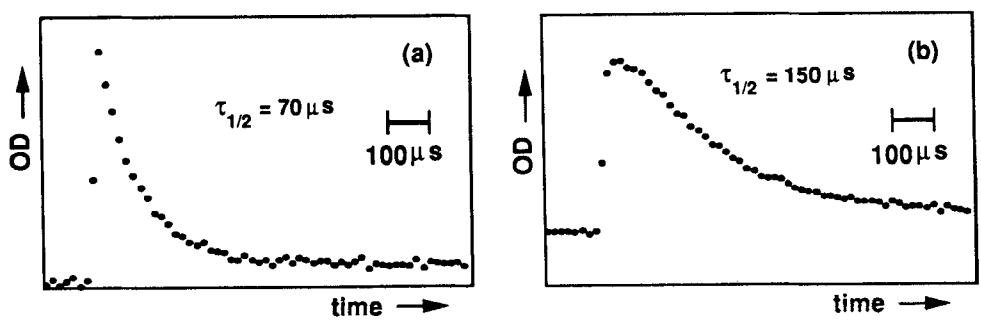
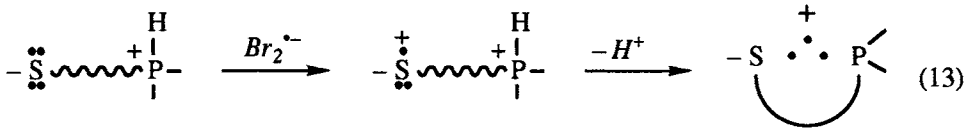


FIGURE 5 Absorption-time traces obtained upon pulse radiolysis of 10^{-4} M solutions of Me–S–$(CH_2)_3$–P–Et_2 in water (N_2O sat.) at pH 8.6 (a) and 4.0 (b). (Measurements at 385 nm).

With a typical 1-electron oxidant, such as $Br_2^{\bullet -}$, formation of the three-electron bonded $(-S\therefore P<)^+$ radical cation is observed both in basic and acid solution. Under the latter condition oxidation can only occur at sulfur (corresponding to the second oxidation step in the electrochemical experiments). Stabilization of the radical cation is then achieved by deprotonation of the phosphonium function.



(13)

At very low pH (≤ 3) deprotonation at phosphorus does not occur anymore, and the sulfur-centered radical cation site stabilizes by association with a sulfur from an unoxidized molecule to yield the $(>S\therefore S<)^+$ three-electron bonded dimer radical cation.

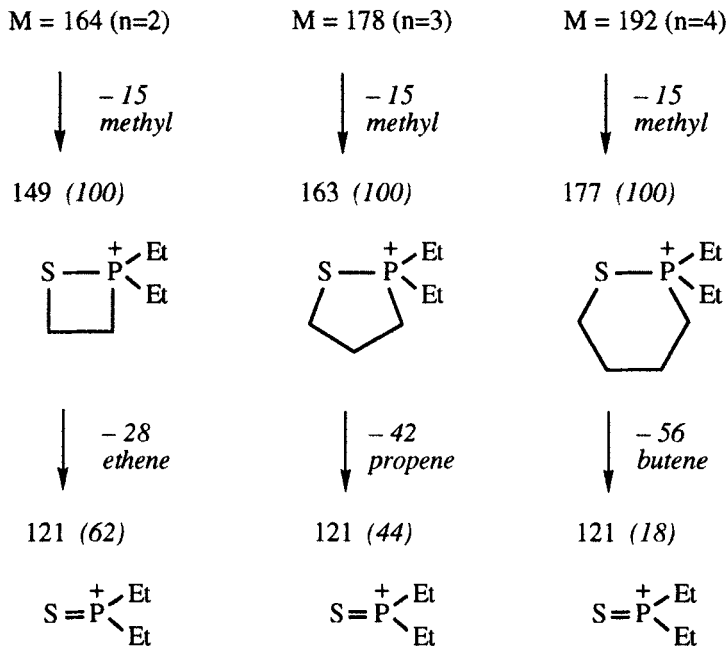
Both the electrochemical oxidation potentials as well as the optical transitions of the three-electron bonded radical cations respond very sensitively to electronic and structural parameters. This is demonstrated with a series of n=3 compounds in which only the nature of the aliphatic substituent R, located at sulfur, is changed. The results are summarized in Table V.

$E_{p,ox}$ and λ_{max} are seen to increase with increasing electron induction by the alkyl substituent. In case of the optical transitions this is well established for many other three-electron bonded species and has been rationalized by an increased electron density in the antibonding σ^* orbital which drives the two interacting heteroatoms further apart. As an immediate consequence the σ/σ^* splitting narrows and causes the observed red-shift in the absorption.[1] By the same token, an increasing electron density at sulfur results in less "lone pair-lone pair" interaction in the unoxidized molecule and consequently lower lying σ^* energy level. The energy necessary to remove the antibonding electrons would accordingly rise (for analogy see Figure 3). Linear free energy plots (not shown here) establish a reasonably linear relationship between the first $E_{p,ox}$ or λ_{max} and Taft's inductive parameter (σ^*) for the smaller and unbranched substituents while deviations, indicating even lesser sulfur-phosphorus orbital interactions, are noticed for s-butyl and particularly t-butyl. This is considered to reflect a steric hindrance exerted by these bulkier substituents, found also in the corresponding series of purely sulfur-centered three-electron bonded radical cations.[1,13]

TABLE V First oxidation peak potentials for $RS(CH_2)_3PEt_2$, and λ_{max} for the respective *intra*molecular radical cations upon one-electron oxidation by $^{\bullet}OH$ radicals.

R	1. peak	λ_{max} $(S\therefore P)^+$
Me	0.370 V	385 nm
Et	0.380 V	396 nm
Pr	0.400 V	392 nm
n-Bu	0.420 V	400 nm
s-Bu	0.475 V	410 nm
t-Bu	0.713 V	430 nm

SCHEME Mass spectrometry of $MeS(CH_2)_nPEt_2$ (EI, 70 eV); relative abundances in parentheses after mass number, e.g. *(100)*.



Experimental evidence for "lone pair - lone pair" interaction in the unoxidized molecules is finally also provided by mass spectrometry. Ionization of $MeS(CH_2)_nPEt_2$ (n=2-4) results in base peaks which indicate loss of the methyl group from the molecular moiety. (The molecular cations could not be observed). In a secondary step the bridging $(CH_2)_n$ units are lost, presumably as alkene (possibly cyclo-alkane), leaving in all cases the diethylthiophosphonyl. The suggested processes are depicted in the above scheme. Particularly the formation of the transient phosphonium cations, in which the phosphorus is linked to the sulfur, are taken as an indication for a pre-existing S–P interaction in the unoxidized molecules.

Conclusion

The one- and two-electron oxidations of 1,ω-bis-(methylthio)alkanes, 1-(methylthio)-ω-(methylseleno)alkanes, 1,ω-bis-(methylseleno)alkanes, and 1-(alkylthio)-ω-(diethylphosphino)alkanes, have been studied by pulse radiolysis and cyclic voltammetry, respectively. The one-electron process yields radical cations with a three-electron ($2\sigma/1\sigma^*$) bond between the two *intra*molecularly linked hetero atoms. The electrochemical data provide direct evidence for a strong "lone pair - lone pair" interaction between the heteroatoms in the unoxidized ground state.

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