Aqueous Phase One-Electron Reduction of Sulfonium, Selenonium and Telluronium Salts

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Keywords: Radicals / One-electron reduction / Sulfonium salts / Selenonium salts / Telluronium salts

Triorganylsulfonium, -selenonium and -telluronium salts were reduced by carbon dioxide radical anions/solvated electrons produced in aqueous solution by radiolysis. The radical expulsion accompanying reduction occurred with the expected leaving group propensities (benzyl > secondary alkyl > primary alkyl > methyl > phenyl), although greater than expected loss of the phenyl group was often observed. Diorganyl chalcogenides formed in the reductions were conveniently isolated by extraction with an organic solvent. Product yields based on the amount of reducing radicals obtained from the γ-source were often higher than stoichiometric (up to 1800 %) in the reduction of selenonium and telluronium compounds; it is likely that this result can be accounted for in terms of a chain reaction with carbon-centred radicals/formate serving as the chain transfer agent. The product distribution was essentially independent of the reducing species for diphenyl alkyl telluronium salts, whereas significant variations were seen for some of the corresponding selenonium salts. This would suggest the intermediacy of telluranyl radicals in the one-electron reduction of telluronium salts. However, pulse radiolysis experiments indicated that the lifetimes of such a species (the triphenyltelluranyl radical) would have to be less than 1 μs.

Introduction

Currently, there is a trend in chemistry to develop "clean" methodology for carrying out various types of transformations.[1,2] Rather than using complex reagents that could give rise to toxic by-products, the main aspiration of this "green chemistry" is to induce reactions by simple energy transfer. If solvents are required, they should be environmentally benign. In this context, the powerful one-electron reductants (essentially the solvated electron and the hydrogen atom) produced by radiolysis of water would seem interesting for carrying out various kinds of reduction reactions. Under γ-radiolysis conditions, a steady-state concentration of reducing equivalents prevails, and the rate of radical production is 5 to 8 orders of magnitude lower than in pulse radiolysis. If the aqueous solution is saturated with N_2O and sodium formate is added, solvated electrons are first converted into oxidizing hydroxyl radicals (Eq. 1)and then, together with hydrogen atoms, transformed into the reducing (E_{red} = –1.9 V[3]) carbon dioxide radical anion (Eq. 2). This species is less potent as a reducing agent than the solvated electron (E_{red} = –2.9 V). If required, a 1:1 mixture of the solvated electron and the carbon dioxide radical anion can be conveniently generated by radiolysis of an argon-saturated aqueous solution of sodium formate.

$$e_{aq}^{-} + N_2O \xrightarrow{H_2O} HO\cdot + HO^{-} + N_2 \qquad (1)$$

$$HO\cdot/H\cdot + HCO_2^{-} \rightarrow CO_2^{-\cdot} + H_2O/H_2 \qquad (2)$$

Reduction of triorganyl onium salts of sulfur, selenium and tellurium is followed by rapid decomposition to form diorganyl chalcogenides and a carbon-centred radical (Eq. 3). We thought that one-electron reductants produced by radiolysis of water could be useful for cleanly effecting such transformations. Chemical reduction of onium species, by the use of potassium graphite, for example,[4] is known to give rise to rather complex mixtures due to further reactions (coupling, disproportionation, hydrogen abstraction and alkyl transfer) of the primarily formed carbon-centred radicals. The question of whether this reaction is concerted or proceeds via a stepwise mechanism has been much investigated and debated.[5] If electron transfer (ET)[6] is concerted with breaking of the chalcogen–carbon bond (inner sphere ET), the mechanism is reduced to that of an S_N2 reaction (Eq. 3, path A). If, on the other hand, the electron transfer is separated from the subsequent step involving cleavage of the bond to the leaving group, the reduction may be classified as outer sphere ET (path B).

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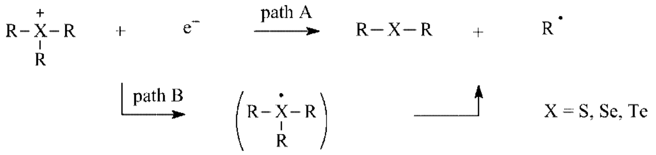
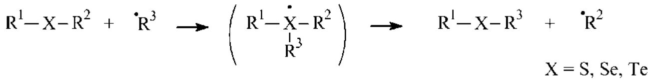


(3)

A large variety of sulfonium salts have been reduced by chemical,[4,7–8] electrochemical,[9–12] photochemical[13–17] or pulse radiolytic methods.[18] In general, carbon–sulfur bond cleavage is found to occur irreversibly and leaving group propensity parallels radical stability (benzyl > secondary > primary > methyl > phenyl). At a time resolution of 0.1 µs there is no experimental evidence for the intermediacy of a sulfuranyl intermediate.[18,19] However, Savéant and coworkers have demonstrated cases of reduction in which the concerted or stepwise character of the ET bond-breaking process appears to be related both to molecular structure[11] and the way in which electron transfer is effected.[17]

The one-electron reduction of selenonium and telluronium salts has received only scant attention. A selenuranyl radical intermediate was proposed for the reduction of some cyclic selenonium salts with magnesium or Grignard reagents,[20,21] whilst sulfuranyl,[22–24] selenuranyl[25] and telluranyl[25,26] radicals have also been invoked as intermediates in homolytic substitution at sulfur, selenium and tellurium (Eq. 4). High-level calculations based on pseudopotential basis sets and electron correlation suggested that the transient species involved in the methyl radical displacement at methanetellurol (Eq. 4; $R^1 = R^3 = Me$; $R^2 = H$; $X = Te$) is an intermediate lying 23.5 kJ mol^{-1} above the reactants.[27] On the other hand, the similar reactions at selenium and sulfur were predicted to proceed via symmetrical transition states with barriers of 63.1 and 87.9 kJ mol^{-1}, respectively.



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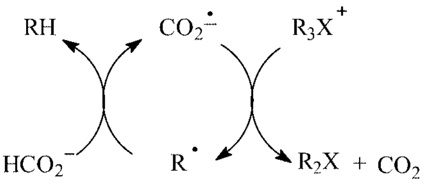
In view of the many interesting aspects of sulfonium, selenonium and telluronium ion reduction, we thought it would be interesting to carry out a comparative study using the one-electron reductants produced in aqueous solution by radiolysis.

Results and Discussion

The powerful one-electron reductants produced by radiolysis of water turned out to be excellent reducing agents for water-soluble onium salts of sulfur, selenium and tellurium. A typical reduction experiment involved γ-radiolysis of a 5×10^{-4} M solution of the onium salt for 6–30 min, extraction of the resulting cloudy (due to formation of insoluble diorganyl chalcogenide) aqueous solution with pentane, and gas chromatographic analysis of the products formed. In one series of experiments (Table 1) the carbon dioxide radical anion was the principal reductant generated. In another series of experiments (Table 1) approximately equal amounts of the carbon dioxide radical anion and the more strongly reducing solvated electron were generated. The organochalcogen products formed during homogeneous-phase reduction of various alkyl diphenyl onium salts **1**–**11** of sulfur, selenium and tellurium (Eq. 5) are shown inTable 1. The product yields based on the amount of reducing radicals obtained from the γ-source were often higher than stoichiometric (up to 1800 %) in the reduction of selenonium and telluronium compounds (entries 2, 3, 6, 7, 11, 16, 17). In contrast, sulfonium compounds were frequently incompletely reduced. This suggests a chain reaction in the reduction of onium salts of the two heavier chalcogens, with sodium formate serving as the hydrogen atom donor (Eq. 6). Apparently, the phenyl radical is the best chain transfer agent (Table 1, entries 2 and 3). Benzene was detected by GC in the reduction of onium salts **1**–**3** and was quantified in one case (entry 2); the yield (86 %) was in close agreement with that for diphenyl selenide. We believe that a chain reaction could also be operative for sulfonium salts, but the reduction of the salts may be too slow for the process to be efficient. For example, under the ordinary reduction conditions, no diphenyl ethyl sulfonium tetrafluoroborate was reduced. On the other hand, when the reduction was performed in argon-saturated, aqueous propan-2-ol (0.1 M) containing sodium formate and sodium hydroxide, stoichiometric amounts (Table 1, entry 8) of reduction products were isolated. Five times the stoichiometric amount of reduction products (based on the amount of reducing radicals) was formed when the reduction was carried out in N_2O-purged aqueous propan-2-ol (0.1 M) containing sodium hydroxide (Table 1, entry 9).

$$\overset{+}{Ph_2XR} \xrightarrow[H_2O]{\text{reduction}} Ph_2X + PhXR + RH/PhH \qquad (5)$$



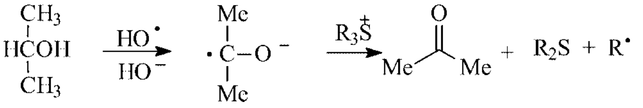
(6)

Apparently, the deprotonated 2-hydroxy-2-propyl radical anion formed under these conditions (Eq. 7) is an efficient reducing agent for sulfonium salts (E_{red} = –2.1 V[3]) and propan-2-ol can act as a hydrogen atom donor for radicals produced to allow a chain reaction to be operative.

Table 1. Aqueous phase reduction of onium salts[a] of sulfur, selenium and tellurium

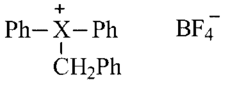
Entry	Compd.	R	X	Reducing agent[b]	Ph_2X (%)[c]	PhXR (%)[c]	Ph_2X/PhXR ratio	Reduction yield (%)[d]
1	**1**	phenyl	S	$CO_2^{-\cdot}$	10	–	–	45
2	**2**	phenyl	Se	$CO_2^{-\cdot}$	91	–	–	1800
3	**3**	phenyl	Te	$CO_2^{-\cdot}$	81	–	–	1400
4	**4**	methyl	Se	$CO_2^{-\cdot}$	2	29	1:12	140
5	**4**	methyl	Se	$CO_2^{-\cdot}/e_{aq}^-$	4	26	1:6.0	130
6	**5**	methyl	Te	$CO_2^{-\cdot}$	77	21	3.7:1	360
7	**5**	methyl	Te	$CO_2^{-\cdot}/e_{aq}^-$	71	19	3.7:1	340
8	**6**	ethyl	S	$(CH_3)_2CO^{-\cdot}$	14	44	1:3.1	110
9	**6**	ethyl	S	$(CH_3)_2CO^{-\cdot}$	17	73	1:4.4	500
10	**7**	ethyl	Se	$CO_2^{-\cdot}$	38	26	1.5:1	220
11	**7**	ethyl	Se	$CO_2^{-\cdot}/e_{aq}^-$	29	28	1:1	300
12	**8**	ethyl	Te	$CO_2^{-\cdot}$	44	0	1:0	160
13	**8**	ethyl	Te	$CO_2^{-\cdot}/e_{aq}^-$	45	0	1:0	170
14	**9**	cyclohexyl	Se	$CO_2^{-\cdot}$	67	13	5.2:1	150
15	**9**	cyclohexyl	Se	$CO_2^{-\cdot}/e_{aq}^-$	43	9	5.1:1	100
16	**10**	cyclohexyl	Te	$CO_2^{-\cdot}$	84	11	7.8:1	350
17	**10**	cyclohexyl	Te	$CO_2^{-\cdot}/e_{aq}^-$	85	12	7.8:1	360
18	**11**	benzyl	Te	$CO_2^{-\cdot}$	24	0	2.4:1[e]	130
19	**11**	benzyl	Te	$CO_2^{-\cdot}/e_{aq}^-$	27	0	2.4:1[e]	110

[a] Except in the case of compounds **1**–**3** (chlorides), the counterion is tetrafluoroborate. [b] Carbon dioxide radical anion: γ-radiolysis of the onium salt in an aqueous sodium formate solution (0.1 M) saturated with N_2O. Carbon dioxide radical anion/solvated electron: γ-radiolysis of the onium salt in an aqueous sodium formate solution (0.1 M) saturated with Ar. Deprotonated 2-hydroxy-2-propyl radical: In entry 8 the reduction was performed in an aqueous solution containing sodium formate (0.16 M) and propan-2-ol (0.1 M) with addition of NaOH (1 mM). The solution was saturated with argon prior to irradiation. In entry 9 the reduction was performed in an aqueous solution containing sodium hydroxide (1 mM) and propan-2-ol (0.1 M) saturated with N_2O prior to irradiation. [c] Yield based on the amount of onium salt and determined by gas chromatography. [d] Yield of chalcogen-containing products based on the amount of reducing radicals obtained from the γ-source (this is related to the irradiation time). [e] Ph_2X/bibenzyl ratios are given.



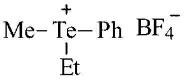
(7)

For the alkyl diphenyl telluronium salts investigated, efficient chain reactions were also seen for the methyl and cyclohexyl derivatives (Table 1, entries 6/7 and 16/17). In the former case, chain transfer is likely to occur by hydrogen abstraction by methyl, whilst in the latter case reduction of the telluronium compound by the cyclohexyl radical seems more likely. However, no attempts were made to detect cyclohexene thus formed. On reduction, benzyl diphenyl telluronium tetrafluoroborate (**11**,Table 1) and the corresponding sulfur and selenium compounds **12** and **13** expelled the benzyl radical exclusively. For thermodynamic reasons (low bond dissociation energy of the benzylic C–H bond) this species is unlikely to abstract hydrogen from formate. Accordingly, toluene was never detected and bibenzyl was always formed as a product of dimerization. Surprisingly, the $Ph_2X/PhCH_2CH_2Ph$ ratio was much larger than expected in the reduction of sulfonium compound **12** and selenonium compound **13**,and the yield based on reducing equivalents was larger than expected for the selenonium compound. These apparently conflicting results are due to competing hydrolysis of these onium salts, thus generating diaryl chalcogenide by a non-radical pathway, under the experimental conditions. In contrast to compounds **12** and **13**, the other onium salts investigated were stable towards hydrolysis for at least one hour in aqueous sodium formate (0.1 M).



$Ph-\overset{+}{X}(CH_2Ph)-Ph \quad BF_4^-$

12 X=S
13 X=Se



$Me-\overset{+}{Te}(Et)-Ph \quad BF_4^-$

14

As an example of a telluronium compound carrying three different substituents, ethyl methyl phenyl telluronium tetrafluoroborate (**14**) was reduced by the carbon dioxide radical anion or the mixture of carbon dioxide radical anion/solvated electron. The product of phenyl expulsion, the volatile ethyl methyl telluride, could not be analysed with any certainty in this case. Ethyl radical expulsion was more prevalent than methyl expulsion, and the methyl phenyl telluride/ethyl phenyl telluride ratios in the two experiments were found to be 3.8:1 and 3.4:1, respectively. The reduction yields based on the amount of reducing radical were close to 200 % in both cases.

With some exceptions, the leaving group propensities observed during homogeneous phase reduction of diphenyl onium salts of sulfur, selenium and tellurium were as expected (benzyl > secondary > primary > methyl > phenyl). In agreement with earlier findings during chemical reduction of diphenyl alkyl sulfonium ions,[4] greater than expected loss of the phenyl group was observed. This was especially true for the reduction of the diphenyl methyl selenonium ion. The expulsion of a larger phenyl radical would relieve strain in the transient species involved in the reduction reaction. On the other hand, diphenyl ethyl telluronium ion showed only loss of ethyl radical on reduction.

The principal reducing agents present during reduction of onium salts are the carbon dioxide radical anion or an equal amount of this species and the solvated electron. Were these reactions to proceed via intermediates, one would expect the product distributions to be independent of the reduction conditions (Eq. 3, path B). On the other hand, if electron transfer were concerted with breaking of the chalcogen–carbon bond, the product distribution would depend on the reducing agent employed (Eq. 3, path A). From the examples presented in Table 1, it would seem that in the case of telluronium salts the product distribution is more or less independent of the reducing agent, whereas significant variations are seen for some selenonium salts (entries 4/5 and 10/11). This could indicate the intermediacy of telluranyl radicals in the one-electron reduction of telluronium salts. However, when aqueous solutions of triphenyltelluronium chloride (**3**) or triphenylsulfonium chloride (**1**) containing *tert*-butyl alcohol as a scavenger of hydroxyl radicals were pulse-irradiated in air, a signal at 490 nm was detected in both experiments. The new peak was formed within 5×10^{-5} s and then disappeared in a second-order reaction with a rate of 10^9 M^{-1} s^{-1}. These results indicate that a phenyl radical is cleaved off from the onium salts to form a phenylperoxyl radical almost immediately after reduction (aryl peroxyl radicals are formed in the reaction between aryl radicals and molecular oxygen and they absorb at 490–600 nm[28]) and then undergoes recombination. Future work, employing laser flash photolysis techniques, would hopefully prove useful in the detection of short-lived (< 1 μs) telluranyl radicals.

A signal observed at 280 nm in the reduction of triphenyltelluronium chloride under oxygen-free conditions is likely to be due to diphenyl telluride. In the presence of sodium formate, this signal increased by a factor of 15. From the large absorbance it is concluded that a chain reaction also occurs on the pulse radiolysis scale (i.e. tenths of a μs). The chain length increased with increasing concentration of the telluronium salt.

In conclusion, the one-electron reductants produced in aqueous solution by radiolysis have been shown to reduce sulfonium, selenonium and telluronium salts conveniently and cleanly with expulsion of the most stable radical species. Chain reactions were often observed, with the radical species/formate serving as the chain-transfer agents.

Experimental Section

Diphenyl diselenide, diphenyl disulfide and diphenyl sulfide are commercially available. Diphenyl selenide was obtained from the Eastman Kodak company. Diphenyl ditelluride,[29] diphenyl telluride,[30] triphenylsulfonium chloride,[31] triphenylselenonium chloride[32] and triphenyltelluronium chloride[33] were prepared by literature procedures. Diphenyl ethyl sulfonium tetrafluoroborate,[34] diphenyl benzyl sulfonium tetrafluoroborate[34] and diphenyl benzyl telluronium tetrafluoroborate[35] were prepared by the procedure described by Franzen.[34] Diphenyl methyl telluronium tetrafluoroborate[36] and ethyl methyl phenyl telluronium tetrafluoroborate[37] were prepared by literature methods. The following materials were prepared in analogy with published procedures (alkyl aryl selenides[38] and tellurides[39]) and were used as reference compounds in the GC analyses: cyclohexyl phenyl selenide,[40] cyclohexyl phenyl telluride,[41] ethyl phenyl sulfide,[42] ethyl phenyl selenide,[43] ethyl phenyl telluride,[44] methyl phenyl selenide[45] and methyl phenyl telluride.[44]

Preparation of Onium Tetrafluoroborate Salts. Typical Procedure: Diphenyl Methyl Selenonium Tetrafluoroborate (4): $AgBF_4$ (0.86 g, 98 %, 4.30 mmol) was slowly added to a mixture of diphenyl selenide (1.00 g, 4.30 mmol) and methyl iodide (6.10 g, 43 mmol) under N_2 at ambient temperature. After the mixture had been stirred for 17 h in the dark, CH_2Cl_2 (50 mL) was added and the reaction mixture was filtered. The filtrate was dried ($CaCl_2$) and concentrated to afford an oil, which crystallized upon treatment with ether. After recrystallization (ether/CH_2Cl_2), the title compound (1.18 g, 87 %) was obtained as white crystals, m.p. 119–121 °C. ^{1}H NMR $\delta = 7.59$ (m, 4 H), 7.68 (m, 6 H), 3.40 (s, 3 H). $C_{13}H_{13}BF_4Se$ (335.0): C, 46.61; H, 3.91. Found: C, 46.79; H, 3.82.

The following compounds were prepared analogously from the corresponding chalcogenides and the appropriate iodo compounds.

Diphenyl Ethyl Selenonium Tetrafluoroborate (7): Yield 64 %, m.p. 66–66.5 °C. ^{1}H NMR $\delta = 7.59$–7.74 (several peaks, 10 H), 4.06 (q, $J = 7.4$ Hz, 2 H), 1.53 (t, $J = 7.3$ Hz, 3 H). $C_{14}H_{15}BF_4Se$ (349.0): C, 48.18; H, 4.33. Found: C, 48.01; H, 4.24.

Diphenyl Ethyl Telluronium Tetrafluoroborate(8): Yield 45 %, oil. ^{1}H NMR $\delta = 7.51$–7.65 (several peaks, 10 H), 3.58 (q, $J = 7.6$ Hz, 2 H), 1.50 (t, $J = 7.5$ Hz, 3 H). $C_{14}H_{15}BF_4Te$ (397.7): C, 42.28; H, 3.80. Found: C, 41.48; H, 3.39.

Cyclohexyl Diphenyl Selenonium Tetrafluoroborate (9): Yield 51 %, m.p. 151–153 °C. ^{1}H NMR $\delta = 7.85$ (m, 4 H), 7.67 (m, 6 H), 4.86 (m, 1 H), 2.08 (m, 2 H), 1.21–1.51 (several peaks, 8 H). $C_{18}H_{21}BF_4Se$ (403.1): C, 53.63; H, 5.25. Found: C, 53.85; H, 5.10.

Cyclohexyl Diphenyl Telluronium Tetrafluoroborate(10): Yield 21 %, m.p. 146–147 °C. ^{1}H NMR $\delta = 7.56$–7.77 (several peaks, 10 H), 4.28 (m, 1 H), 2.17 (m, 2 H), 1.24–1.90 (several peaks, 8 H). $C_{18}H_{21}BF_4Te$ (451.8): C, 47.86; H, 4.69. Found: C, 47.72; H, 4.58.

Benzyl Diphenyl Selenonium Tetrafluoroborate(13): Yield 26 %, m.p. 122–123 °C. ^{1}H NMR $\delta = 7.53$–7.62 (several peaks, 10 H),7.19–7.27 (several peaks, 5 H), 5.24 (s, 2 H). $C_{19}H_{17}BF_4Se$ (411.1): C, 55.51; H, 4.17. Found: C, 55.55; H, 4.12.

GC analyses were performed on a Varian 3400 GC fitted with a capillary Rescom SE 54 column and a flame ionization detector. Calibration curves were made for benzene, methyl phenyl telluride, diphenyl sulfide, diphenyl selenide and diphenyl telluride with pentadecane as internal standard. For all other compounds, a response factor vs. the corresponding diphenyl chalcogenides was determined and used for calculation of the product ratios.

Pulse radiolysis was performed at room temperature (22–23 °C) with the use of doses of 2–15 Gy per pulse, corresponding to 1.2–9×10^{-6} mol dm^{-3} of radicals. The 7 MeV microtron accelerator[46] and the computerized optical detection system[47] have been described elsewhere. The cell used had an optical path length of 1 cm. Dosimetry was performed by use of an aerated KSCN solution (10^{-2} mol dm^{-3}) taking[48] $G\varepsilon = 2.23 \times 10^{-4}$ m^2 J^{-1} at 500 nm. γ-Radiolysis was carried out in a ^{60}Co γ-source at a dose of 0.27 Gy s^{-1} (corresponding to 0.6×10^{-5} mol e$^-$ + OH min^{-1} dm^{-3}) as determined by the Fricke dosimeter.[48] Irradiation times ranged from 6 to 60 min.

Typical Procedure: Triphenylselenonium chloride (**2**; 0.0239 g, 1.64×10^{-5} mol) was dissolved in Millipore-deionized water

(50 mL) containing sodium formate (0.1 M) in a reaction flask possessing a gas inlet through a glass frit and a gas outlet. The solution was purged with N_2O for 5 min, stoppered and irradiated in the γ-source for 12 min. The cloudy aqueous solution was then extracted with pentane (3 × 15 mL) and the organic phase was analysed by gas chromatography.

Acknowledgments

Financial support by the Swedish Research Council is gratefully acknowledged.

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Received: August 26, 2004