Pulse Radiolysis of para-Substituted Phenyl Selenides and Tellurides in Methanolic Solution. I

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The pulse radiolysis of \( \text{Ar}_2\text{Se} \), \( \text{Ar}_2\text{Se}_2 \), \( \text{Ar}_2\text{Te} \) and \( \text{Ar}_2\text{Te}_2 \) (\( \text{Ar} = \text{p}-\text{methoxyphenyl} \)) in neutral and acid methanolic solution permitted the observation of transients assigned to the radicals \( \text{ArSe}^- \), \( \text{ArSeSe}^- \) and \( \text{ArTe}^- \).

Hydrogen atoms react with both mono- and diselenide producing the same radical \( \text{ArSe}^- \) and solvated electrons react with monoselenide producing \( \text{ArSe}^- \) through an acid catalyzed reaction.

For the diselenide two reaction modes are proposed, one producing \( \text{ArSe}^- \) and the other \( \text{ArSeSe}^- \). In mono- and ditelluride solution only the \( \text{ArTe}^- \) radical was observed.

Reliable studies on organoselenium and organotellurium radicals have only recently been made. Thus Chu et al. found evidence for the formation of the radicals \( \text{C}_x\text{H}_y\text{C}_z\text{H}_w\text{Se}^- \) and \( \text{C}_x\text{H}_y\text{C}_z\text{H}_w\text{SeSe}^- \) during the photolysis of benzyl diselenide and Marsh et al. proposed an organotellurium radical fragment in the photodecomposition of bis(benzoyl)methyltellurium dichloride.

In this paper we report the results from pulse radiolysis of \( \text{Ar}_2\text{Se} \) and \( \text{Ar}_2\text{Se}_2 \) (\( \text{Ar} = \text{p}-\text{methoxyphenyl} \)) and the corresponding tellurides in methanolic solution. Evidence for the formation of radicals of the type \( \text{ArSe}^- \), \( \text{ArTe}^- \) and \( \text{ArSeSe}^- \) was obtained.

EXPERIMENTAL

The selenium and tellurium compounds were synthesized as described below. Melting points were determined on a micro hot stage and are uncorrected. Mass spectra were obtained with an LKB 9000 A instrument using the direct inlet technique. The electron energy was 70 eV. \( \text{SeOCl}_2 \) (Merck), \( \text{TeCl}_4 \) (Merck) and \( \text{KSeCN} \) (BDH) were used as received.

\( \text{Ar}_2\text{Se} \) and \( \text{Ar}_2\text{Te} \) were synthesized from \( \text{Ar}_2\text{SeCl}_2 \) and \( \text{Ar}_2\text{TeCl}_2 \) respectively, according to Bergman. The preparation of \( \text{Ar}_2\text{SeCl}_2 \) was carried out according to Alqvist with some modifications. A solution of \( \text{SeOCl}_2 \) (16.6 g, 0.1 mol) and anisole (21.6 g, 0.2 mol) in dry ether (100 ml) was stirred for 20 h, at 25 °C. After concentration the solid formed was collected, washed with cold ether, dried and recrystallized from ethanol. Yield: 91%, m.p. 159–160 °C (lit. 163 °C). \( \text{Ar}_2\text{TeCl}_2 \) was synthesized according to Bergman. \( \text{ArSeCN} \) was prepared as described by Behagel. MS, \( m/e \) (rel. intensity) 215 (6), 213 (31), 211 (16), 210 (6), 209 (6), 187 (9), 172 (5), 170 (7), 144 (5), 134 (10), 133 (100), 103 (10). Only peaks above \( m/e \) 100 and stronger than 4% of the base peak are listed.

\( \text{Ar}_2\text{Se} \) was prepared using the method of Rheinboldt and Giesbrecht with some modifications. \( \text{ArSeCN} \) (1 g) was stirred for 5 h in 2 M \( \text{NaOH} \) (25 ml), at 25 °C. The solid formed was collected, dried and recrystallized from ethanol. It is important that the \( \text{ArSeCN} \) is pure. If not, the crude diselenide is very difficult to purify. Yield 80%, m.p. 49.5–50.0 °C (lit. 50.7–51.6 °C). MS, \( m/e \) (rel. intensity) 376 (14), 375 (7), 374 (42), 373 (9), 372 (38), 371 (15), 370 (23), 369 (7), 368 (9), 214 (10), 199 (5), 189 (19), 188 (10), 187 (100), 186 (7), 185 (50), 184 (19), 183 (20), 172 (18), 170 (9), 144 (12), 142 (6). Only peaks above \( m/e \) 100 and stronger than 4% of the base peak are listed.

\( \text{Ar}_2\text{Te} \) was synthesized from \( \text{ArTeCl}_3 \) by reduction with hydrazine.

The methanol used as solvent (Fluka, p.a.) was distilled in a packed column after addition of 2,4-dinitrophenylhydrazine and \( \text{H}_2\text{SO}_4 \). The solutions were freed from oxygen by purging with \( \text{Ar} \) (Aga SR-quality) for half an hour. The \( \text{N}_2\text{O} \) (Aga) was

used as received. The solutions were acidified with 
H₂SO₄ (Merck, p.a.).
The accelerator and pulse radiolysis set up are 
described elsewhere.¹⁰,¹¹ The irradiation cell used 
was of 2 cm optical path length. Conductivity 
measurements could be started 0.5 µs after electron 
pulse.

RESULTS AND DISCUSSION

About 10⁻⁹ s after the radiation induced decom-
position of methanol the main products are CH₂O, 
·CH₂OH, e⁻ and H⁺. The G-values are G(CH₂O· + 
·CH₂OH) = 2.5, G(e⁻ + H⁺) = 3.7 and G(e⁻) = 1.3.¹² 
CH₂O· is converted into ·CH₂OH within 10⁻⁷ s. 
On addition of H⁺ or N₂O the solvated electrons 
(e⁻) are converted into H⁺ or ·CH₂OH radicals, 
respectively.

The transient absorption spectra obtained from 
pulse irradiated solutions of Ar₂Se and Ar₂Se₂ are 
shown in Fig. 1. In acid (5 × 10⁻³ mol dm⁻³ H₂SO₄) 
and neutral Ar₂Se solutions an absorption with 
maximum at 535 nm was obtained. In acid Ar₂Se₂ 
solutions a more intense but otherwise identical 
absorption was obtained, whereas in neutral solu-
tion a shoulder on the low energy side of the 
spectrum with absorption maximum at ~600 nm 
appeared immediately after the electron pulse. This 
absorption was found to decay much slower than 
the 535 nm absorption. The transient decayed 
without the formation of any optically observable 
products in the wavelength range 420–650 nm. 
On N₂O-saturating neutral and slightly acid (5 × 
10⁻⁷ mol dm⁻³ H₂SO₄) 0.87 × 10⁻² mol dm⁻³ 
methanolic solutions of Ar₂Se the absorption 
intensity at 535 nm decreased by a factor of 2.5 and 
2.33, respectively, (Table 1) clearly indicating that 
the 535 nm absorption must be assigned to a 
radical/radical ion with both the solvated electron 
and H⁺ as precursors. The plot of 1/OD at 535 nm 
versus 1/C(Ar₂Se) in pulse irradiated acid solution 
(10⁻² mol dm⁻³ H⁺) (Fig. 2) gives a straight line. 
From the intercept of this plot we obtain Gₑ = 9000 
whereas in acid solution of Ar₂Se₂ Gₑ was found to 
be concentration independent in the concentration 
range (10⁻⁴–10⁻³) mol dm⁻³ and equal to 14 700. 
No change in electrical conductivity was detected 
in slightly acid or neutral solutions of Ar₂Se.

To accommodate the experimental results we 
assign the 535 nm absorption to the only possible 
common uncharged selenium centered radical ArSe⁻ 
and propose the reactions.

\[
e⁻ + \text{Ar}_2\text{Se} \xrightarrow{k_i} \text{ArSe}⁻ + \text{ArH} 
\]

\[(1)\]

H· + ArSe ArSe· + ArH \hspace{1cm} (2)

According to this mechanism ODAr/ODN_{2}O at 535 nm equals the ratio \([G(e^{-}) + G(H)]/G(H)\) when all e^{-} and H· react with ArSe. From Fig. 2 it is estimated that in \(0.87 \times 10^{-2}\) mol dm\(^{-3}\) ArSe solution \(\sim 38\%\) of all H· radicals react with ArSe. Taking this into account and using the G-values given above ODAr/ODN_{2}O is calculated to be 2.43 which is in very good agreement with the values 2.5 and 2.33 obtained from the experimental data in Table I.

The kinetic plot in Fig. 2 is explained by the competition between reactions (2) and (3)

\[
H· + CH_{3}OH \rightarrow H_{2} + \cdot CH_{2}OH \hspace{1cm} (3)
\]

and from the slope we obtain \(k_{2}/k_{3} = 1.36 \times 10^{3}\). Assuming \(k_{3} = 1.6 \times 10^{9}\) M\(^{-1}\) s\(^{-1}\), the rate constant \(k_{2}\) is calculated to be \((2.2 \pm 0.2) \times 10^{9}\) M\(^{-1}\) s\(^{-1}\).

The transient absorptions in acid \((5 \times 10^{3}\) mol dm\(^{-3}\) H\(_{2}\)SO\(_{4}\)\) 1.5 \times 10\(^{-5}\) mol dm\(^{-3}\) ArSe solution 2 and 15 \(\mu s\) after pulse irradiation are shown in Fig. 3. The absorption with maximum at 305 nm is assigned to a cyclohexadienyl type radical and the rate constant for the reaction of \(\cdot CH_{2}OH\) with ArSe is estimated from the growing in of the 305 nm and the decay of the \(\cdot CH_{2}OH\) absorption to be \(\sim 10^{9}\) M\(^{-1}\) s\(^{-1}\).

The two absorption bands obtained in neutral ArSe\(_{2}\) solutions are suggestive of two reaction modes according to reactions (4) and (5) and we assign the 600 nm absorption to the radical ArSe\(_{2}e^{-}\).

\[
e^{-} + ArSe_{2} \rightarrow CH_{3}OH.H^{+} \rightarrow ArSe + ArSeH \hspace{1cm} (4)
\]

\[
\rightarrow ArSeSe^{+} + ArH \hspace{1cm} (5)
\]

Using Baxendale's and Mellows\(^{12}\) methanol data \(G(H^{+} + e^{-}) \sim 3.7 G(\text{sacvengable radicals}) \sim 6.5\) and the ratio of the experimental G-values \(\sim 1.63\) in acid solution at least \(83\%\) of all accessible radicals other than hydrogen atoms were found to react with ArSe\(_{2}\) to give ArSe\(_{2}e^{-}\) i.e. the hydroxymethyl radical reacts according to eqn. (6).

\[
\cdot CH_{2}OH + ArSe_{2} \rightarrow ArSe_{2}e^{-} + \text{prod.} \hspace{1cm} (6)
\]

The decay of the 535 nm absorption in ArSe solutions follows pseudo first-order kinetics and from the plot in Fig. 4 of the observed first-order rate constant versus ArSe concentration the rate constant of reaction 7 was found to be \(k_{7} = 8 \times 10^{5}\) M\(^{-1}\) s\(^{-1}\).
Fig. 4. The observed rate constant for the reaction
ArSe⁺ + Ar₂Se → prod. vs. Ar₂Se concentration
(kₗ = 8 × 10⁵ M⁻¹ s⁻¹).

ArSe⁺ + Ar₆Se → prod.

(7)

The fact that the straight line in Fig. 4 does not pass through origo indicates competition between reaction (7) and second-order reactions at low Ar₂Se concentration.

Fig. 5. Transient spectra in pulse irradiated Ar₃Te₂ and Ar₂Te solution in O, methanol; ●, cyclohexane.

Fig. 6. Ge at 508 nm in pulse irradiated methanolic Ar₂Te solutions vs. Ar₂Te concentration.

In acid and neutral methanolic solutions of the corresponding tellurides and ditellurides a transient absorption with maximum at 508 nm and a small shoulder on the high energy side of the spectrum (λ ~ 490 nm) was obtained (Fig. 5). In cyclohexane, however, a transient absorption with no shoulder and the maximum shifted to 498 nm was obtained. The absorptions are assigned to the tellurium centered radical ArTe⁺.

A plot of 1/Ge at 508 nm versus 1/C(Ar₂Te) in pulse irradiated solutions gives a straight line in accordance with the competition between reactions (8) and (3).

H⁺ + Ar₂Te → ArTe⁺ + ArH

(8)

From the intercept and slope of the plot in Fig. 6 the rate constant is calculated to be kₖ = 1.5 × 10¹⁰ M⁻¹ s⁻¹.

The Ge values were found to be the same in methanolic solutions of both telluride and ditelluride. This clearly indicates that the hydroxymethyl radicals react very slowly or not at all with Ar₂Te₂.

Acknowledgement. The financial support by the Swedish Atomic Research Council is gratefully acknowledged.
REFERENCES


Received December 27, 1977.