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

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The pulse radiolysis of Ar₂Se, Ar₂Se₂, Ar₂Te and Ar₂Te₂ (Ar = *p*-methoxyphenyl) in neutral and acid methanolic solution permitted the observation of transients assigned to the radicals ArSe·, ArSeSe· and ArTe·.

Hydrogen atoms react with both mono- and diselenide producing the same radical ArSe· and solvated electrons react with monoselenide producing ArSe· through an acid catalyzed reaction.

For the diselenide two reaction modes are proposed, one producing ArSe· and the other ArSeSe·. In mono- and ditelluride solution only the ArTe· radical was observed.

Reliable studies on organoselenium and organotellurium radicals have only recently been made.^{1–3} Thus Chu *et al.*² found evidence for the formation of the radicals C₆H₅CH₂Se· and C₆H₅CH₂SeSe· during the photolysis of benzyl diselenide and Marsh *et al.*¹ proposed an organotellurium radical fragment in the photodecomposition of bis(benzoylmethyl)tellurium dichloride.

In this paper we report the results from pulse radiolysis of Ar₂Se and Ar₂Se₂ (Ar = *p*-methoxyphenyl) and the corresponding tellurides in methanolic solution. Evidence for the formation of radicals of the type ArSe·, ArTe· and 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. SeOCl₂ (Merck),

TeCl₄ (Merck) and KSeCN (BDH) were used as received.

Ar₂Se and Ar₂Te were synthesized from Ar₂SeCl₂ and Ar₂TeCl₂ respectively, according to Bergman.⁴ The preparation of Ar₂SeCl₂ was carried out according to Alqvist⁵ with some modifications. A solution of SeOCl₂ (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.⁵ 163 °C). Ar₂TeCl₂ was synthesized according to Bergman.⁴ ArSeCN was prepared as described by Behagel.⁶ 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.

Ar₂Se₂ was prepared using the method of Rheinboldt and Giesbrecht⁷ with some modifications. ArSeCN (1 g) was stirred for 5 h in 2 M NaOH (25 ml), at 25 °C. The solid formed was collected, dried and recrystallized from ethanol. It is important that the ArSeCN is pure. If not, the crude diselenide is very difficult to purify. Yield 80 %, m.p. 49.5–50.0 °C (lit.⁸ 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.

Ar₂Te₂ was synthesized from ArTeCl₃⁹ by reduction with hydrazine.⁴

The methanol used as solvent (Fluka, *p.a.*) was distilled in a packed column after addition of 2,4-dinitrophenylhydrazine and H₂SO₄. The solutions were freed from oxygen by purging with Ar (Aga SR-quality) for half an hour. The N₂O (Aga) was

Fig. 1. Transient absorptions in pulse irradiated methanolic solutions of Ar_2Se and Ar_2Se_2 . $\square$, $\sim 10^{-2} \text{ mol dm}^{-3}$ Ar_2Se in acid ($0.5 \times 10^{-3} \text{ mol dm}^{-3} \text{H}_2\text{SO}_4$) and neutral solution. Dose: 3.3 krad. $\sim 10^{-3} \text{ mol dm}^{-3}$ Ar_2Se_2 , neutral solution; ∇ , immediately after electron pulse; $\triangle$, 40 μs after electron pulse; Dose: 2.40 krad.

used as received. The solutions were acidified with H_2SO_4 (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 decomposition of methanol the main products are $\text{CH}_3\text{O}\cdot$, $\cdot\text{CH}_2\text{OH}$, e_s^- and $\text{H}\cdot$. The G -values are $G(\text{CH}_3\text{O}\cdot + \cdot\text{CH}_2\text{OH}) = 2.5$, $G(\text{e}_s^- + \text{H}\cdot) = 3.7$ and $G(\text{e}_s^-) \approx 1.3$.¹² $\text{CH}_3\text{O}\cdot$ is converted into $\cdot\text{CH}_2\text{OH}$ within 10^{-7} s. On addition of H^+ or N_2O the solvated electrons (e_s^-) are converted into $\text{H}\cdot$ or $\cdot\text{CH}_2\text{OH}$ radicals, respectively.

The transient absorption spectra obtained from pulse irradiated solutions of Ar_2Se and Ar_2Se_2 are

Table 1. Effect of proton concentration and N_2O on intensity of the transient absorption at 535 nm on pulse radiolysis of $0.87 \times 10^{-2} \text{ mol dm}^{-3}$ methanolic solution of Ar_2Se . Dose 3.6 krad.

C_{H^+} mol dm^{-3}	Purging gas	OD_{235}	$(\text{OD}_{\text{Ar}}/\text{OD}_{\text{N}_2\text{O}})$
1.2×10^{-2}	Ar	0.012(1)	
Neutral	Ar	0.010(1)	2.5
Neutral	N_2O	0.004(1)	
10^{-6}	Ar	0.014(1)	2.33
10^{-6}	N_2O	0.006(1)	

In alkaline methanol an irreversible decomposition of the selenium compound seems to take place.

shown in Fig. 1. In acid ($5 \times 10^{-3} \text{ mol dm}^{-3} \text{H}_2\text{SO}_4$) and neutral Ar_2Se solutions an absorption with maximum at 535 nm was obtained. In acid Ar_2Se_2 solutions a more intense but otherwise identical absorption was obtained, whereas in neutral solution 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 N_2O -saturating neutral and slightly acid ($5 \times 10^{-7} \text{ mol dm}^{-3} \text{H}_2\text{SO}_4$) $0.87 \times 10^{-2} \text{ mol dm}^{-3}$ methanolic solutions of Ar_2Se 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 $\text{H}\cdot$ as precursors. The plot of $1/\text{OD}$ at 535 nm versus $1/C(\text{Ar}_2\text{Se})$ in pulse irradiated acid solution ($10^{-2} \text{ mol dm}^{-3} \text{H}^+$) (Fig. 2) gives a straight line. From the intercept of this plot we obtain $G\varepsilon = 9000$ whereas in acid solution of Ar_2Se_2 $G\varepsilon$ 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 Ar_2Se .

To accommodate the experimental results we assign the 535 nm absorption to the only possible common uncharged selenium centered radical $\text{ArSe}\cdot$ and propose the reactions.

Fig. 2. $1/G(535 \text{ nm})$ in pulse irradiated methanolic solutions of Ar_2Se vs. $1/C(\text{Ar}_2\text{Se})$.

According to this mechanism $\text{ODAr}/\text{OD}_{\text{N}_2\text{O}}$ at 535 nm equals the ratio $[G(e_s^-) + G(\text{H})]/G(\text{H})$ when all e_s^- and $\text{H}\cdot$ react with Ar_2Se . From Fig. 2 it is estimated that in $0.87 \times 10^{-2} \text{ mol dm}^{-3}$ Ar_2Se solution $\sim 38\%$ of all $\text{H}\cdot$ radicals react with Ar_2Se . Taking this into account and using the G -values given above $\text{ODAr}/\text{OD}_{\text{N}_2\text{O}}$ 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 1.

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

and from the slope we obtain $k_2/k_3 = 1.36 \times 10^3$. Assuming $k_3 = 1.6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ¹³ the rate constant k_2 is calculated to be $(2.2 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

The transient absorptions in acid ($5 \times 10^3 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$) $1.5 \times 10^{-5} \text{ mol dm}^{-3} \text{ Ar}_2\text{Se}$ solution 2 and 15 μs after pulse irradiation are shown in in Fig. 3. The absorption with maximum at 305 nm is assigned to a cyclohexadienyl type radical and

Fig. 3. Transient absorption in pulse irradiated $1.5 \times 10^{-5} \text{ mol dm}^{-3}$ acid ($5 \times 10^{-3} \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$) solution of Ar_2Se . $\circ$, 2 μs after electron pulse; $\square$, 15 μs .

the rate constant for the reaction of $\cdot\text{CH}_2\text{OH}$ with Ar_2Se is estimated from the growing in of the 305 nm and the decay of the $\cdot\text{CH}_2\text{OH}$ absorption to be $\sim 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

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 $\text{ArSeSe}\cdot$.

Using Baxendales and Mellows¹² methanol data $G(\text{H}\cdot + e_s^-) \sim 3.7$ $G(\text{scavengable radicals}) \sim 6.5$ and the ratio of the experimental G -values ~ 1.63 in acid solution at least 83% of all accessible radicals other than hydrogen atoms were found to react with Ar_2Se_2 to give $\text{ArSe}\cdot$, i.e. the hydroxymethyl radical reacts according to eqn. (6).

The decay of the 535 nm absorption in Ar_2Se solutions follows pseudo first-order kinetics and from the plot in Fig. 4 of the observed first-order rate constant versus Ar_2Se concentration the rate constant of reaction 7 was found to be $k_7 = 8 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$.

Fig. 4. The observed rate constant for the reaction $\text{ArSe}\cdot + \text{Ar}_2\text{Se} \rightarrow \text{prod.}$ vs. Ar_2Se concentration ($k_7 = 8 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$).

The fact that the straight line in Fig. 4 does not pass through origin indicates competition between reaction (7) and second-order reactions at low Ar_2Se concentration.

Fig. 5. Transient spectra in pulse irradiated Ar_2Te_2 and Ar_2Te solution in $\circ$, methanol; $\bullet$, cyclohexane.

Fig. 6. $G\epsilon$ at 508 nm in pulse irradiated methanolic Ar_2Te solutions vs. Ar_2Te 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 ($\lambda \sim 490 \text{ nm}$) 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 $\text{ArTe}\cdot$.

A plot of $1/G\epsilon$ at 508 nm versus $1/C(\text{Ar}_2\text{Te})$ in pulse irradiated solutions gives a straight line in accordance with the competition between reactions (8) and (3).

From the intercept and slope of the plot in Fig. 6 the rate constant is calculated to be $k_8 = 1.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.

The $G\epsilon$ -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 Ar_2Te_2 .

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