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# Reaction of Mono- and Dihaloalkanes with Mixed Solutions of Chalcogens in Alkaline Reductive Systems

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**Abstract**—Sufur–selenium, sulfur–tellurium, selenium–tellurium, and sulfur–selenium–tellurium mixtures readily dissolve in the hydrazine hydrate–alkali system to form chalcogenide anions. Alkylation of the latter with ethyl bromide results in preferential formation of diethyl disulfide, diethyl diselenide, and diethyl ditelluride. Tellurium reacts with dichloromethane in the presence of sulfur, yielding poly(methylene ditelluride), the reaction in the presence of selenium gives rise to poly(methylene selenotellurides), while in the sulfur–selenium–tellurium mixture polymers containing all the components are formed.

Polymers with chalcogenide bridges in the chain are used as photoactive cationic materials for electrophotography [1–4].

We earlier showed that elemental chalcogens are activated by such an alkaline reductive system as hydrazine hydrate–alkali; therewith, alkali metal mono- or polychalcogenides are generated under mild conditions [5, 6]. Moreover, we introduced into the alkaline reductive system, in succession or simultaneously, sulfur and selenium. It was found that on dissolution of sulfur followed by selenium or of a mixture of sulfur and selenium in the $NaOH(KOH)–N_2H_4–H_2O–H_2O$ mixture, mixed alkali metal sulfoselenides are generated along with mono- and polysulfides and polyselenides. The formation of mixed alkali metal sulfoselenides was detected in the alkylation of the $S–Se–NaOH(KOH)–N_2H_4–H_2O–H_2O$ system with ethyl bromide. The alkylation of selenium solutions or mixed sulfur and selenium solutions with dihaloalkanes affords poly(methylene diselenides) or mixed poly(alkylene sulfoselenides) [7, 8].

Proceeding with these studies, we have explored the possibility of generation in alkaline reductive systems of mixed selenotelluride, sulfotelluride, and sulfoselenotelluride anions and their subsequent alkylation with mono- and dihaloalkanes.

Into a solution of sodium hydroxide in hydrazine hydrate we introduced in succession sulfur and tellurium, selenium and tellurium, or sulfur and selenium, and tellurium. The solutions were heated at 85–90°C for 1.5 h, cooled, and treated with ethyl bromide. The reaction conditions and compositions and the yields of the resulting compounds are listed in Table 1. For the sake of comparison, we also give data for reactions of mixtures of sulfur and selenium in similar

**Table 1.** Alkylation with ethyl bromide of chalcogen solutions in the hydrazine hydrate (30–40 ml)–NaOH system (35°C)

| Initial reagents, g | | | Conversion of EtBr, % | Reaction products, g | Yields of reaction products, % (per reacted EtBr) |
|---|---|---|---|---|---|
| chalcogens | NaOH | EtBr | | | |
| S, 1.6; Se, 4.9 | 4.0 | 10.9[a] | 98.0 | 6.5 | 2.2 ($Et_2S$), 5.5 ($Et_2Se$), 29.7 ($Et_2S_2$), 36.2 ($Et_2Se_2$), 25.9 ($Et_2SSe$) |
| S, 3.2; Te, 12.8 | 8.0 | 21.8 | 97.7 | 10 | 3.5 ($Et_2S$), 21.3 ($Et_2S_2$), 4.7 ($Et_2Te$), 37.2 ($Et_2Te_2$), 5.0 ($Et_2STe$) |
| S, 4.2; Te, 9.0 | 8.0 | 21.8 | 98.0 | 6 | 2.2 ($Et_2S$), 24.9 ($Et_2S_2$), 2.7 ($Et_2Te$), 27.0 (Et2Te2), 2.1 ($Et_2STe$) |
| Se, 7.8; Te, 12.8 | 8.0 | 21.8 | 85.0 | 12 | 5.3 ($Et_2Se$), 43.7 ($Et_2Se_2$), 3.5 ($Et_2Te$), 30.3 ($Et_2Te_2$), 1.03 ($Et_2SeTe$) |
| S, 2.1; Se, 5.2; Te, 8.4 | 8.0 | 21.8 | 85.0 | 11 | Traces ($Et_2S$), 4.6 ($Et_2Se$), 15.5 ($Et_2S_2$), 24.0 ($Et_2Se_2$), 7.9 ($Et_2Te$), 14.4 ($Et_2Te_2$) |

[a] The synthesis was performed in water; volume of hydrazine hydrate 3 ml.

conditions [8]. The reaction products were identified by GLC using authentic samples, as well as by GC–MS. The mass spectra contain the molecular ions of the resulting diethyl chalcogenides, including mixed ones whose authentic samples were unavailable.

Unlike the S–Se system, the S–Te system in the alkaline reductive system generates little $STe^-$ (yield of diethyl sulfotelluride 5%). The major reaction products here are diethyl disulfide and diethyl ditelluride, as well as small amounts of diethyl sulfide and diethyl telluride.

$$S + Te + 2\ NaOH + N_2H_4\cdot H_2O$$

$$\xrightarrow{2EtBr} \underset{3.5\%}{Et_2S} + \underset{4.7\%}{Et_2Te} + \underset{21.3\%}{Et_2S_2} + \underset{5.0\%}{Et_2STe} + \underset{37.3\%}{Et_2Te_2}.$$

At the S : Te molar ratio increased to 2, the yields of the mixed and ditelluride anions decrease.

Mixed anions are even worse generated on activation in the alkaline reductive system of a mixture of selenium and tellurium.

$$Se + Te + 2NaOH + N_2H_4\cdot H_2O$$

$$\xrightarrow{2EtBr} \underset{5.3\%}{Et_2Se} + \underset{3.5\%}{Et_2Te} + \underset{43.7\%}{Et_2Se_2} + \underset{1.03\%}{Et_2SeTe} + \underset{30.3\%}{Et_2Te_2}.$$

With a 1 : 1 : 1 mixture of the three chalcogenides in the hydrazine hydrate–alkali system, only one mixed sulfoselenide anion is formed in a low yield, whereas the major anions formed are diselenide, as well as dislfide and ditelluride.

$$S + Se + Te + 3NaOH + N_2H_4\cdot H_2O$$

$$\xrightarrow{2EtBr} \underset{4.6\%}{Et_2Se} + \underset{7.9\%}{Et_2Te} + \underset{15.5\%}{Et_2S_2} + \underset{24.0\%}{Et_2Se_2} + \underset{2.7\%}{Et_2SSe} + \underset{14.4\%}{Et_2Te_2}.$$

Thus, mixed anions are best formed from sulfur and selenium, worse from sulfur and tellurium, and very bad from selenium and tellurium. The reactions of mixtures of sulfur and selenium are performed in water, and hydrazine hydrate is taken in a stoichiometric amount as reducer. The other chalcogenides are activated in hydrazine hydrate only. We took these results into accout in alkylation of chalcogenides with dihaloalkanes and preparation of polymers with different chalcogenide bridges.

We studied the synthesis of chalcogenide polymers by alkylation with dihaloalkanes with selenium or tellurium in alkaline reductive systems. It was found that polymers are formed only when the selenium solution is alkylated with dichloromethane [7] or 1-bromo-3-chloropropane. At the same time, 1,2-dichloro- and 1,2-dibromomethanes, 1,4-dibromobutane, and 1,5-dichloropentane do not work in any conditions. Probably, these alkylating agents undergo alkaline dehydrohalogenation to give ethylene, 1,3-butadiene, and 1,4-pentadiene, respectively.

Tellurium fails to react with dielectrophiles in these systems. At the same time, the S–Te, Se–Te, and S–Se–Te binary and ternary systems are alkylated with dichloromethane, yielding polymers. The reaction conditions and polymer compositions are given in Table 2.

Sulfur and tellurium in an aqueous hydrazine hydrate–NaOH system do not react with dichloromethane. However, this reaction occurs in hydrazine hydrate as medium and reducer and gives a polymer (black adhesive substance) which, according to its elemental analysis, contains mostly ditelluride bridges. The approximate formula $C_3H_{14}S_{0.5}Te_7$ may correspond to the following polymer.

$$S + Te + 2NaOH + Na_2H_4\cdot H_2O \xrightarrow{CH_2Cl_2} Cl\left[CH_2TeTeCH_2TeTeCH_2TeTeCH_2STeCH_2TeTeCH_2TeTeCH_2TeTe\right]_n CH_2Cl.$$

A certain excess of hydrogen atoms is presumably explained by the presence in the polymer chain of tetravalent tellurium atoms bound by hydrogen atoms. The directions of alkylation of a mixture of sulfur and tellurium in alkaline reductive systems with mono- and dihaloalkanes are much different. Dichloromethane, unlike ethyl bromide, prefers to react with ditelluride anions and, apparently, fully binds sulfotelluride anions. Therewith, poly(methylene ditellurides) that have little sulfotelluride bridges acquire stability in alkaline reductive systems (from tellurium alone no polymer is formed). Similarly, selenium is alkylated with 1,2-dichloroethane only in the presence of sulfur [8].

The reaction of dichloromethane with a mixture of selenium and tellurium in the hydrazine hydrate–NaOH system takes another pathway. The polymer formed (black substance) comprises much selenium and tellurium and has the formula $C_3H_{15}Cl_{0.2}Se_4Te_5$.

**Table 2.** Alkylation with dichloromethane of chalcogens in the hydrazine hydrate–NaOH system (35–40°C)[a]

| Initial reagents, g | | | | Reaction time, h | Polymer yield, g | Found, % | Formula | Calculated, % |
|---|---|---|---|---|---|---|---|---|
| chalcogens | NaOH | $N_2H_4 \cdot H_2O$ ($H_2O$), ml | dihalide | | | | | |
| S, 1.6; Te, 6.4 | 4.0 | 10 (30) | $CH_2Cl_2$, 8.4 | 5 | 0 | | | |
| S, 1.6; Te, 6.4 | 4.0 | 40 | $CH_2Cl_2$, 8.4 | 8 | 5 | C 3.14; H 1.41; S 1.4; Te 91.98 | $C_3H_{14}S_{0.5}Te_7$ | C 3.76; H 1.46; S 1.67; Te 93.08 |
| Te, 12.8 | 4.0 | 40 | $CH_2Cl_2$, 8.4 | 6 | 11.1 (Te) | | | Te 100 |
| Se, 3.9; Te, 6.38 | 4.0 | 40 | $CH_2Cl_2$, 8.4 | 2 | 8.5 | C 3.73; H 1.57; Cl 0.88; Se 30.7; Te 62.69 | $C_3H_{15}Cl_{0.2}Se_4Te_5$ | C 3.56; H 1.4; Cl 0.69; Se 31.28; Te 62.87 |
| S, 1.2; Se, 2.73; Te, 4.48 | 4.0 | 30 | $CH_2Cl_2$, 8.4 | 2 | 2.5 | C 5.72; H 0.83; Cl 0.5; S 7.35; Se 20.2; Te 55.6 | $C_5H_8Cl_{0.1}S_2Se_{2.5}Te_4$ | C 7.1; H 0.9; Cl 0.4; S 7.6; Se 23.48; Te 60.4 |
| Se, 7.8 | 4.0 | 1.5 | $CH_2Cl_2$, 12.8 (0.2) | 1.5 | 8 | C 4.6; H 1.0; Cl 7.6; Se 86.22 | $C_2H_5ClSe_5$ | C 5.2; H 1.0; Cl 7.7; Se 85.96 |
| Se, 3.9 | 2.0 | 3 | $ClCH_2CH_2Cl$, 9.8 | 0.1 | [b] | | | |
| Se, 2.9 | 1.0 | 12.5 | $BrCH_2CH_2Br$, 7.01 | 0.5 | [b] | | | |
| Se, 7.8 | 4.0 | 1.5 | $ClCH_2CH_2 \cdot CH_2Br$, 7.9 | 0.1 | 9.4 | C 14.16; H 3.24; Cl 1.09; Se 78.94 | $C_3H_8Cl_{0.1}Se_3$ | C 12.74; H 2.81; Cl 1.23; Se 83.3 |
| Se, 7.8 | 4.0 | 1.5 | $Br(CH_2)_4Br$, 10.8 | 0.1 | [b] | | | |
| Se, 7.8 | 4.0 | 1.5 | $Cl(CH_2)_5Cl$, 7.05 | 0.1 | [b] | | | |

[a] All mixed poly(methylene chalcogenides) are black bright adhesive substances, poly(methylene diselenide) is a dark claret rubber-like substance, and poly(propylene diselenide) is a solid dark orange substance. [b] Polymer is not formed.

This result suggests that the polymer chain contains mostly diselenide and ditelluride bridges.

$$Se + Te + 2NaOH + Na_2H_4 \cdot H_2O \xrightarrow{CH_2Cl_2} Cl\left[CH_2TeTeCH_2TeTeCH_2SeSeCH_2SeSe\right]_nCH_2Cl.$$

Mixed selenotelludie bridges are unlikely here, since selenotelluride anions are scarcely formed in this system. Selenotelluride polymers contain even more excess hydrogen that sulfoteluride polymers. This may also result from Te–H bond formation in the polymer chain. Dichloromethane, like ethyl bromide, effectively binds ditelluride and diselenide anions.

A mixture of sulfur, selenium, and tellurim in the hydrazine hydrate–NaOH system, too, is alkylated with dichloromethane to give a black adhesive polymer. Its composition $C_5H_8Cl_{0.1}S_2Se_{2.5}Te_4$ corresponds to the following structure.

$$S + Se + Te + 2NaOH + Na_2H_4 \cdot H_2O \xrightarrow{CH_2Cl_2} Cl\left[CH_2TeTeCH_2TeTeCH_2SeSeCH_2SSCH_2Se\right]_nCH_2Cl.$$

Dichloromethane alkylates the S + Se + Te mixture, preferentially binding ditelluride anions. A few mixed sulfoselenide bridges, too, may be present in the polymer chain. The IR spectrum of the resulting polymer shows the following frequencies, $cm^{-1}$: 1445, 1376, 1125 [$\nu(CH_2)$], 770 [$\delta(CH_2)$], 630 (C–Te), 570

(Se–Se), 580 (Te–Te), 490 (S–S, S–Se).

Thus, we found that sulfur–selenium, sulfur–tellurium, selenium–tellurium, and sulfur–selen–tellurium mixtures in alkaline reductive systems form different chalcogenide anions. These anions are readily alkylated with monohaloalkanes, such as ethyl bromide. The major alkylation products are diethyl disulfide, diethyl diselenide, and diethyl ditelluride. Mixed diethyl chalcogenides are best formed from sulfur and selenium, worse from sulfur and tellurium, and very bad from selenium and tellurium. Individual chalcogens or their mixtures differently react in with dihaloalkanes in alkaline reductive systems. Tellurium in the system hydrazine hydrate–alkali fails to react with dichloromethane but reacts with the latter in the presence of sulfur. Therewith, sulfur scarcely takes part in reaction and acts to stabilize poly(methylene ditelluride) in alkaline reductive systems. In the presence of selenium, tellurium, too, is alkylated with dichloromethane, forming mixed poly(methylene selenotellurides) with alternating ditelluride and diselenide bridges. Ditelluride anions, too, prefer to bind with dichloromethane in the presence of selenium and sulfur. The resulting polymer contains ditelluride, diselenide, and, apparently, disulfide bridges (sulfoselenide bridges may also be present). The developed simple procedures for synthesis of poly(methylene chalcogenides) make use of available chalcogens and hydrazine hydrate–alkali system.

## EXPERIMENTAL

The IR spectra of the polymers were obtained on an IFS-25, Sample Scant-250 instrument in KBr or thin films. The mass spectra of the alkylation products were obtained on an LKB-2091 GC–MS system, ionization energy 57 eV, gas chromatography was performed on an SB-5 capillary column (25 m).

Analysis of the alkylation products of solutions of sulfur and selenium with ethyl bromide was performed by GLC on an LKhM-8MD-2 chtomatograph in the linear programming mode (12 deg/min) using a stainless-steel column (1000 × 3 mm) packed with 5% of XE-60 on Chromaton N-AW-HMDS, carrier gas helium.

**Mixed diethyl chalcogenides** (Table 1). Chalcogens were successively added in portions to a solution of NaOH in hydrazine hydrate at 27°C until they dissolved completely. The reddish-orange solution was heated at 85–90°C for 1.5 h, cooled to room temperature, and ethyl bromide was added. The reaction mixture warmed up to 35°C (this temperature was further maintained) and decolorized. After cooling, the lower organic layer was separated, washed with water, dried with $CaCl_2$, and subjected to GLC and GC–MS analysis. The yields of the reaction products were estimated by GLC data.

**Poly(alkylene chalcogenides).** Chalcogens were successively added in portions to a solution of NaOH in hydrazine hydrate at 27°C until they dissolved completely. The dark claret solution was heated at 85–90°C for 2 h. After cooling, dihaloalkane was added in protions. The reaction mixture warmed up to 35–46°C and was kept at this temperature for some hours. The polymers that precipitated were washed with water and dried in a vacuum.

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