Tetrahedron Vol. 38, No. 15, pp. 2421 to 2423, 1982
Printed in Great Britain.

0040-4020/82/152421-03$03.00/0
Pergamon Press Ltd.

STUDIES ON THE REACTIONS OF SELENITE ION WITH 1,2-DIMERCAPTOETHANE OR THIOACETIC ACID

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(*Received in the UK* 12 *August* 1981)

Abstract—The reactions are reported between selenite and 1,2-dimercaptoethane (DME) or thioacetic acid (TAA) to form moderately stable derivatives having an enhaced absorptions in the 230–360 nm region in combining molar ratios 3:2 and 4:1, respectively. Both reactions invariably yield one product corresponding to the selenium-containing derivative of DME or TAA. The formation of products is a pH dependent process. The equilibrium constants of reactions between selenite and DME or TAA were measured.

The reaction of aqueous solutions of thiols with selenite yielding relatively unstable derivatives has been known for 40 years.[1-5] Painter[2] assumed the reaction between thiols and selenite to proceed in the following way:

$$4RSH + SeO_3^{2-} \rightleftharpoons RS\text{-}Se\text{-}SR + RS\text{-}SR + H_2O + 2OH^- \quad (1)$$

Compounds of type RS–Se–SR can be considered as analogues of trisulphides[6] in which one atom of sulphur has been replaced by selenium and therefore they may be conveniently referred to as selenotrisulphides. The potential importance of selenotrisulphides in biological systems, as well as the interesting chemistry involved, made it desirable to study of the reactions between selenite and other types of sulphur compounds, i.e. dithiols (1,2-dimercaptoethane; DME) and thioacids (thioacetic acid; TAA). In this paper the emphasis was put on the identification of species as obtained from the reactions of selenite with DME or TAA.

EXPERIMENTAL

Selenium dioxide was obtained from Polish POCh works, thioacetic acid was purchased from Fluka AG. Buchs SG. 1,2-dimercaptoethane (Puriss AR) was obtained from Laboratory of Department of Radiochemistry, Moscow University. Radioactive ^{75}Se-selenium obtained from Radioisotope Production and Distribution Centre Świerk, Poland, was used as $Na_2{}^{75}SeO_3$. The specific activity was 424 MBq/mg Se. The purity of DME, TAA and radioactive sodium selenite was determined by high voltage paper electrophoresis and by paper chromatography. The reactions of selenite with DME or TAA were studied in 0.1M sodium acetate solution. The pH of the reaction solutions were adjusted with 1M HCl. The reaction mixtures were analysed by paper chromatography, high-voltage paper electrophoresis and spectrophotometrically with a "Specord UV/VIS" spectrophotometer. Whatman 3MM paper impregnated with 10% solution of paraffin oil in cyclohexane was used for ascending chromatography. Analyzed reaction mixtures (^{75}Se-selenite and DME or ^{75}Se-selenite and TAA) were run during 12 h in formaldehyde/water (7:1 v/v) in darkness. The components of the reaction of ^{75}Se-selenite with DME were separated chromatographically using for running of chromatographic strips (Whatman 3MM) the following solvents: 1-butanol/acetic acid/water (4:1:5 v/v), water, isobutyric acid/water (4:1 v/v), methyl ethyl ketone/propionic acid/water (15:5:6 v/v). Whatman 3MM paper was used for electrophoresis. Radioelectrophoretograms and radiochromatograms were developed with nitroprusside spray or with iodine-azide spray. The distribution of the labelled selenium compounds on radiochromatograms and radioelectrophoregrams were scanned with a 4π G-M radiochromatograph (Packard Model 7201). The IR spectra were taken on a UR-20 Zeiss Jena spectrometer.

RESULTS

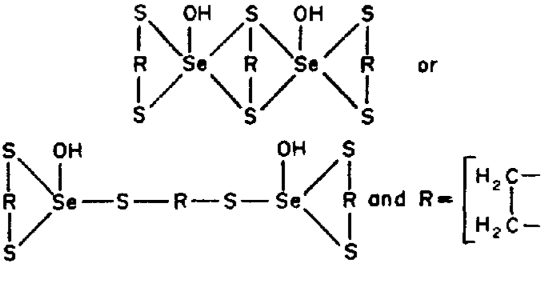
The reaction between ^{75}Se-sodium selenite (3×10^{-5} M) and DME (3×10^{-5} M) was studied at pH 1.5 and 3.8 (at 5°). Two radioactive peaks after 1 h were detected on the radiochromatograms: the first ($R_f = 0$) should be assigned to the product of the selenium incorporation into DME, while the second ($R_f = 0.91$) to the unchanged selenite. The same species were found using for running of chromatographic strips following solvents: formaldehyde/water, 1-butanol/acetic acid/water, water, isobutyric acid/water, methyl ethyl ketone/propionic acid/water. The nitroprusside or iodine-azide spray revealed no spots coinciding with ^{75}Se-peaks. The reaction of ^{75}Se-selenite (6×10^{-5} M) with TAA (8×10^{-5} M) was studied at pH 1.5 and 3.4 (at 5°). Tow radioactive peaks after 1 h were detected: the first should be assigned to the product of the selenium containing derivative of TAA ($R_f = 0.55$), while the second to selenite ($R_f = 0.91$). The nitroprusside or iodine-azide spray revealed no spots coinciding with ^{75}Se-peaks. At pH 5 in the reaction mixture the formation of the colloidal selenium has been observed ($R_f = 0$). It has been also observed that with increasing pH the amount of evolved selenium rises.

The reaction of ^{75}Se-sodium selenite (5.0×10^{-4} M) with DME (1.18×10^{-5} M) was studied at pH 1.4 (at 5°). The obtained results proved the occurrence of only one product of the selenium incorporation into DME. Moreover, the molar ratio of the initial concentration of DME (1.8×10^{-5} M) to reacted selenite (1.17×10^{-5} M) was near 3:2. One product of selenium incorporation into TAA was also found in the reaction mixture of TAA (8×10^{-5} M) with ^{75}Se-selenite (5×10^{-5} M) at pH 1.4 and 3.7 (at 5°). It was found that the equilibrium of both reactions have been established before 50 min of the reactions.

The method of continuous variations[2] used as absorptions of DME, TAA and selenious acid (selenite) in the 255–360 nm region are very small as compared with the absorption of the products of the reactions between selenite and DME or TAA. Spectrophotometric measurements were made after 50 min reaction. The results from measurements at 273 nm argue that the combining molar ratio for DME to selenite is 3:2 (pH of the reaction solutions was 1.7 and 2.9). Assuming the combining molar ratio for DME to selenite to be 3:2 the reaction equation can be written:

$$3\mathrm{DME} + 2\mathrm{SeO_3}^{2-} \overset{K_a}{\rightleftharpoons} [(\mathrm{DME})_3\mathrm{Se_2}](\mathrm{OH})_2 + 4\mathrm{OH}^- \quad (2)$$

where $[(DME)_3Se_2](OH)_2$:



The yield of the product was measured after 50 minutes of the reaction (Table 1). Components were electrophoretically separated. The transition from apparent to real equilibrium constant was made possible with accounting its dependence upon pH:

$$K_a = 1.8 \times 10^{23}\{K_a = K_{pH} \cdot (OH)^{\alpha}, \alpha = -0.46\}$$

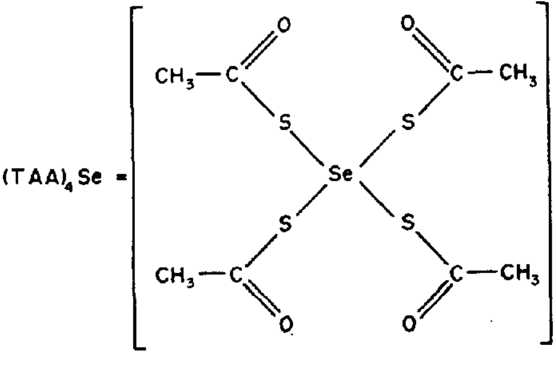
It was found from spectrophotometric measurements (at 258 nm) that the combining molar ratio for TAA to selenite is 4:1 (pH of the reaction solution was 1.5 and 3.4). The combining molar ratio for the reactions cannot be evaluated at pH above 5 for evolving of the colloidal selenium. The latter is due to the decomposition of selenium derivative of DME or TAA. It has been also observed that with increasing of pH and with decreasing of the molecular concentration ratio of selenite to DME or to TAA the rate of evolved selenium rises.

To obtain sufficient of the selenium compound for more complete characterization an aqueous solution of 2×10^{-2} M of SeO_2 in 200 ml of 0.1 M HCl was prepared. To this solution 2×10^{-2} M of DME was added dropwise for 15 min with stirring (at 0°) and the stirring was continued for 20 min in darkness. The yellowish precipitate was collected by filtration, washed with 0.1 M HCl and ethanol, and dried in vacuo over P_2O_5 for 48 h, in darkness at 5° (m.p. 73–78°, with decomposition), found C, 15.49; H, 2.88; $C_6H_{14}O_2S_6Se_2$ requires: C, 15.38; H, 3.01%. The UV spectrum of $[(DME)_3Se_2](OH)_2$ is very similar to spectra of other selenotrisulphides[2,9] confirming that selenium–sulphur bonds (–Se–S– is the chromophore responsible) are present in a molecule of the selenium compound. For this compound the absorption maximum is at 273 nm with a molar extinction coefficient of 5980 $M^{-1}cm^{-1}$. The IR spectrum of $[(DME]_3Se_2](OH)_2$ confirm the existence of O–H and Se–OH bonds. For comparison the infrared frequencies of $[(DME)_3Se_2](OH)_2$ and H_2SeO_3 in the solid state are listed in Table 2. The O–H bonding frequencies in $[(DME)_3Se_2](OH)_2$ and in H_2SeO_3 are rather low for such a hydrogen-bonded system (free OH stretching frequency—about 3700 cm^{-1}).

The aqueous solution containing 0.1M of SeO_2 in 25 ml of 0.1M HCl was prepared. To this solution 0.05M of thioacetic acid was added dropwise for 20 min with shaking and cooling to 0°, and the shaking was continued for 40 min in darkness (at 7°). The organic layer was separated and washed with 0.1M HCl (3 ml). Obtained orange oil was dried (Na_2SO_4) and evaporated. Yield: 2.8 g (70%) found C, 25.51; H, 3.29. $C_8H_{12}O_4Se$ requires: C, 25.32; H, 3.16%. The UV spectrum of $(TAA)_4Se$ is similar to spectra of other selentrisulphides[2,9] confirming that selenium-sulphur bonds are present in a molecule of $(TAA)_4Se$. For this compound the absorption maximum is at 232 nm with $\epsilon = 13350\ M^{-1}cm^{-1}$. The IR spectrum of $(TAA)_4Se$ confirms the existence of C=O bond and the absence of S–H bond. The purity and uniform of obtained compound was determined by paper chromatography. Whatman 3MM strips were placed in an ascending chromatography bath containing water-saturated toluene. The single orange spot was observed. The iodine-azide or nitroprusside spray revealed no spot. Selenium compound showed decomposition when examined by chromatography after three days at 25° or after UV irradiation for 2 h. Consequently the orange spot turned to red-brown. From the experiments a single product of the selenium-containing derivative of TAA was found. So the reaction equation can be written:

$$4\mathrm{TAA} + \mathrm{SeO_3}^{2-} \overset{K_b}{\rightleftharpoons} (\mathrm{TAA})_4\mathrm{Se} + \mathrm{H_2O} + 2\mathrm{OH}^- \quad (3)$$

where:



The yield of product was measured after 50 min of the reaction (Table 3). Components were electrophoretically separated. The transition from apparent to real equilibrium constant was made possible taking account of its pH dependence:

$$K_b = 5.0 \times 10^{25}\{K_b = K_{pH} \cdot (OH)^{\beta}, \quad \beta = -1.12\}.$$

Table 1. The apparent equilibrium constant of the reaction of DME with selenite (at 5°)

pH	DME [M]·10^{-5}	$Na_2{}^{75}SeO_3$ [M]·10^{-5}	$[(DMP)_3{}^{75}Se_2](OH)_2$ [M]·10^{-5}	K_{pH}—the apparent equilibrium constant
1.8	1.792	1.883	0.097	4.8×10^{17}
2.5	1.651	1.698	0.143	1.1×10^{18}
3.7	1.447	1.601	0.281	3.6×10^{18}

Table 2. IR bands of $[(DME)_3Se_2](OH)_2$ (in KBr) and crystalline H_2SeO_3 (frequencies in cm^{-1}).

Ref. 7	Ref. 8	This work	Assignments
1134	1134 ± 1 s	1132	SeOH
1180	1178 ± 2 m	1191	SeOH
2290	2320 ± 15 s	—	O–H
2940	2900 ± 50 vs	3450	O–H

Table 3. The apparent equilibrium constant of the reaction of TAA with selenite (at 5°)

pH	TAA $[M] \cdot 10^{-4}$	$Na_2{}^{75}SeO_3$ $[M] \cdot 10^{-4}$	$(TAA)_4{}^{75}Se$ $[M] \cdot 10^{-4}$	K_{pH}—the apparent equilibrium constant
1.3	11.298	6.099	2.600	2.6×10^{11}
2.9	3.083	4.370	0.736	1.8×10^{13}

CONCLUSION

The present study shows that the reactions of selenite with DME or TAA invariably each yielded one product corresponding to the selenium derivative of DME or TAA. The yield of the reactions (2) and (3) was affected by pH. The earlier view that the combining molar ratio for thiols with selenite is 4:1 has been confirmed for the reaction of TAA with selenite. However, selenite and DME (like 2,3-dimercaptopropanol DMP[9]) react in the molar ratio of 2:3. $[(DME)_3Se_2](OH)_2$ is stable as the isolated solid contrary to selenium derivative of DMP {i.e. $[(DMP)_3Se_2](OH)_2$[9]}. We have found that with increasing pH and with decreasing of the molecular concentration ratio of selenite to DME or to TAA the rate of the decomposition of the selenium derivative of DME or TAA increased. The UV spectra of these selenium compounds and other selenotrisulphides[2,9] are similar, confirming that sulphur-selenium bonds, which are chromophore, are present in a molecule of $[(DME)_3Se_2](OH)_2$ and $(TAA)_4Se$. The chromophore is not a loose complex of the reactants because the experimental points obtained with the method of continuous variations show almost no deviation from the intercept of the two extrapolated lines at the combining ratio. Unexpected $[(DME]_3Se_2](OH)_2$ does not show a much greater absorption than $[(DMP)_3Se_2](OH)_2$ (i.e. $\epsilon = 7360\,M^{-1}\,cm^{-1}$) but the absorption maximum for these both compounds are at 273 nm[9]. Although UV spectra of $[(DME)_3Se_2](OH)_2$ and $(TAA)_4Se$ are similar, $[(DME)_3Se_2](OH)_2$ show the absorption maximum at longer wavelengths than $(TAA)_4Se$ (at 232 nm) or other selenotrisulphides.[2]

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