ACTA CHEMICA SCANDINAVICA 8 (1954) 1351—1356

Iodometric Analysis of Certain Types of Selenenyl Compounds

OLAV FOSS* and SVEN R. SVENDSEN

Universitetets Kjemiske Institutt, Blindern-Oslo, Norway

A rapid and accurate method has been worked out for the iodometric analysis of aromatic selenenyl bromides, thiocyanates, alkoxides and amides.

Some observations have been made on rearrangement reactions involving selenenyl alkoxides and amides.

Selenenyl compounds, with the formulae RSeX where X is an electronegative atom or group, are derivatives of divalent electropositive selenium. In displacement reactions with nucleophilic reagents, the selenium atom acts as the electrophilic part of the molecule [1,2], the atoms or groups X being eliminated as anions. This is analogous to the behaviour of sulphenyl [3] and tellurenyl [4] compounds.

Some years ago, a method was worked out by one of us [3] for the iodometric analysis of aromatic sulphenyl thiocyanates and amides. The procedure was based on the reaction of the sulphenyl compounds with an excess of sodium thiosulphate, to form sulphenyl thiosulphates, and back-titration of the excess of sodium thiosulphate with iodine. The principle of this method has now been found to be appliccable to the iodometric analysis of the analogous selenenyl compounds, and also selenenyl alkoxides and bromides. *o*-Nitrobenzene- and 2,4-dinitrobenzeneselenenyl compounds have been studied, and the results are described below.

Selenenyl compounds react with thiosulphate ion to give the corresponding selenenyl thiosulphates [1]:

$$ArSeX + S_2O_3^{--} = ArSeS_2O_3^- + X^-$$

Here, X may be bromide, thiocyanate, or other electronegative groups the anions of which have a lower nucleophilic reactivity than thiosulphate ion towards divalent selenium. In the case of selenenyl alkoxides and amides,

* Present address: Institutt for uorganisk kjemi, Norges tekniske høgskole, Trondheim, Norway.

where the anions X^- have strong basic properties, an acid must be present in order to neutralize the anions and bring about a complete change:

$$ArSeOR + S_2O_3^{--} + H^+ = ArSeS_2O_3^- + ROH$$
$$ArSeNH_2 + S_2O_3^{--} + 2\ H^+ = ArSeS_2O_3^- + NH_4^+$$

The product, *o*-nitrobenzeneselenenyl thiosulphate, has earlier been isolated as the potassium salt [1] and found to be indifferent to iodine [5]. The same applies to the 2,4-dinitrobenzene analogue, as shown by the results of the present analyses.

The reactions with thiosulphate ion are of interest as a basis for iodometric analysis only if the anions X^- or their neutralization products are indifferent to iodine, so that the excess of sodium thiosulphate can be back-titrated accurately with iodine. This requirement is satisfied for bromides, thiocyanates, alkoxides and amides.

PREPARATION AND PURIFICATION OF COMPOUNDS

The melting points are in °C, and those recorded during the present work are corrected, except for the amides, where the melting points were determined on a Kofler hot bench since the compounds decompose on heating.

o-*Nitrobenzeneselenenyl bromide* was prepared from the selenenyl cyanide and bromine as described by Behaghel and Seibert [6].

2,4-*Dinitrobenzeneselenenyl bromide* was obtained by bromination of the diselenide according to Behaghel and Müller [7]. The diselenide was prepared as follows: 97 g (0.36 mole) of crude 2,4-dinitrobenzeneselenenyl cyanide [8] was suspended in 100 ml of glacial acetic acid; 15 ml (0.18 mole) of pyridine and 7 ml (0.36 mole) of water were added, and the mixture was boiled under reflux for one hour. After cooling, the diselenide was filtered off and washed with ethanol and ether. Yield, 73 g (85 %) of a very pure product.

This is an adaption of Hoggarth and Sexton's method for the preparation of disulphides [9]. The procedure gives a better yield of diselenide and a purer product than methods based on treatment of the selenenyl cyanide with alkalies or sodium acetate.

o-*Nitrobenzeneselenenyl thiocyanate* [1,10] was prepared from the bromide, dissolved in a mixture of ethyl acetate and methanol, by addition of a methanol solution of potassium thiocyanate. This method was used by one of us [1] in the first synthesis of a selenenyl thiocyanate, and has later been employed by Rheinboldt and Perrier [10] for the preparation of a large number of selenenyl thiocyanates. The product is difficult to obtain in a pure state. After four recrystallizations from carbon tetrachloride, the melting point remained practically unchanged; the purity, however, was only 99.2 %, as checked by iodometric analysis. After seven recrystallizations, this figure had increased to 99.6 %. A total number of fifteen recrystallizations were necessary to ensure a product which, according to the thiosulphate-iodine method of analysis, contained no impurities. Melting point, 113.5°; the literature value [10] is 113—114°.

2,4-*Dinitrobenzeneselenenyl thiocyanate* [10] was obtained from the bromide and potassium thiocyanate, as above. This substance had a tendency to decompose when treated with warm carbon tetrachloride for recrystallization in the usual manner, and was purified as follows: About 0.5 g was dissolved, by gentle heating, in 150 ml of carbon tetrachloride, and the filtered solution was cooled in a carbon dioxide-ethanol freezing mixture until part of the liquid had frozen. The beaker and its contents were then allowed to stand at room temperature until the solvent had melted and the selenenyl thiocyanate had changed from a plastic state to a crystalline mass (about two hours). After three such recrystallizations, the melting point was 96.2°, as compared with the literature value [10] of 94—95°. The losses during the recrystallizations were rather large.

The selenenyl *alkoxides* were prepared from the bromides and the appropriate alcohol, by heating under reflux for two hours in presence of an equivalent amount of silver acetate, which serves as a bromide acceptor. This procedure was first used by Behaghel and Müller [7], who believed that selenenyl acetates were formed. The identification of the

products, in the case of the 2,4-dinitrobenzeneselenenyl derivatives, as selenenyl alkoxides, is due to Cook and Donia [11].

o-*Nitrobenzeneselenenyl methoxide* was isolated from the filtered reaction mixture by cooling in a carbon dioxide-ethanol freezing mixture. The product was recrystallized nine times from anhydrous methanol, by cooling as above, and thus appeared as thin, yellow needles which melted at 54.2°. A substance having approximately the same melting point (52°) has been prepared, in the same way, by Behaghel and Müller [7]. Although the latter authors identified the product as o-nitrobenzeneselenenyl acetate, there is no doubt, according to the analytical results given later, that the substance is the methoxide.

o-*Nitrobenzeneselenenyl ethoxide*, isolated as described above for the methoxide, has not been prepared before. It was obtained as small, needle-shaped crystals with a yellow colour. After six recrystallizations from anhydrous ethanol, the solution each time being cooled in a carbon dioxide-ethanol freezing mixture, the substance melted at 26.2°.

The above alkoxides may be obtained from o-nitrobenzeneselenenyl thiocyanate, in the same way as from the bromide. A heating time of 30 minutes was found to be sufficient. In this case, silver thiocyanate is formed, as a side product, instead of silver bromide.

2,4-*Dinitrobenzeneselenenyl methoxide* [11] and the corresponding *ethoxide* [11] were recrystallized three times from the respective anhydrous alcohols. The compounds are readily obtained in a pure state. The melting points were 134.2° for the methoxide and 131° for the ethoxide; Cook and Donia [11] give 131—133° and 128—129°, respectively.

In the recrystallization of selenenyl alkoxides from alcohols, the alcohol corresponding to the alkoxide group contained in the substance must be used; otherwise, rearrangements will take place, as discussed later. Traces of water present may cause decompositions.

o-*Nitrobenzeneselenenyl amide* was prepared from the bromide (5.5 g) dissolved in chloroform (150 ml), by treatment with dry ammonia gas for two hours at room temperature. The ammonium bromide was removed by filtration, and the solvent distilled off *in vacuo*. The crude product was recrystallized five times, by dissolving in carbon tetrachloride, filtering, and cooling in a carbon dioxide-ethanol freezing mixture. The substance is very unstable and could not be obtained in a pure state; the recrystallized product, which melted at about 129°, was by iodometric analysis shown to contain 3.5 % of impurities. The amide probably decomposes into the imide, with liberation of ammonia, as does the corresponding sulphenyl amide [12].

2,4-*Dinitrobenzeneselenenyl amide* was prepared as described above, from 6.5 g of the bromide dissolved in 100 ml of chloroform. After filtering, the chloroform was distilled off at atmospheric pressure, until crystals began to separate out, and the solution was then allowed to cool. Yield, 4.7 g (89 %). After six recrystallizations from chloroform, the substance was analytically pure. The amide appears as orange-coloured prisms which melt at 140°. The crystals decompose slowly when stored at room temperature.

These amides have not been prepared before. The latter amide is formed also when the thiocyanate, dissolved in chloroform, is treated with ammonia gas.

ANALYTICAL PROCEDURE AND RESULTS

The o-nitrobenzene- and 2,4-dinitrobenzeneselenenyl bromides, thiocyanates, alkoxides and amides may be analyzed iodometrically as follows:

About two tenths of a millimole of the substance is weighed into a 250 ml flask, and dissolved, with gentle heating when necessary, in 4 ml of ethyl acetate. 10 ml of 96 % ethanol and 1 ml of glacial acetic acid are added, and then, with a swirling movement of the flask, 25 ml of about 0.01 *N* sodium thiosulphate. After standing for 15 minutes, 100 ml of water and 10 ml of 0.2 % starch solution are added, and the excess of sodium thiosulphate is back-titrated with standard 0.01 *N* iodine.

A blank titration is carried out, with the difference that the glacial acetic acid is added after the dilution with water, not before, and the titration is then performed immediately, in order that the acid shall not decompose the thiosulphate ion, which now is present at a larger concentration.

The difference between the numbers of milliliters of 0.01 *N* iodine consumed in the blank and the real titration gives the amount of selenenyl compound present, in hundredths of millimoles.

The time of standing, before back-titration, may be varied according to the nature of the substance analyzed and the excess of sodium thiosulphate present. The selenenyl bromides and thiocyanates react very rapidly with thiosulphate, and titration can begin immediately after the thiosulphate has been added. The selenenyl amides react slowest, and the time, 15 minutes, is sufficient for these when an excess of about 5 ml of sodium thiosulphate is present.

The thiocyanate ion is indifferent to iodine only in presence of potassium iodide [13]. The amount of iodide introduced during the titrations were found to be sufficient for this purpose.

The selenenyl thiosulphates, which occur as products, form yellowish green solutions. The end point in the titrations, when starch is used as an indicator, might therefore be thought to be observed a little late relative to the blank titrations, where the selenenyl thiosulphate is not present. The results, however, indicate that this is not the case, if care is taken in observing the end point.

The period of drainage of the pipet, on delivery of the sodium thiosulphate, should be a little longer than usual, due to the effect of the ethyl acetate-ethanol vapours.

The ethyl acetate used as a solvent had been distilled over iodine in order to remove small amounts of oxidable impurities. The 0.01 *N* sodium thiosulphate solution was prepared fresh every day by dilution from a 0.1 *N* stock solution. The 0.01 *N* iodine solution was made up with 2 % of potassium iodide, in order to depress effectively the volatility of iodine. As a result of this relatively large amount of potassium iodide, the titer value decreased by 0.4 % only in the course of nine weeks. The solution was standardized against reagent grade arsenous oxide.

The weighings were performed on a micro balance, and the back-titration volumes of iodine were read on a 10 ml micro buret.

The results for those compounds which, by this method, were judged analytically pure, are given in Tables 1 and 2. It appears that the method gives consistent and accurate results. The average deviation from the theoretical

Table 1. Iodometric analysis of o-nitrobenzeneselenenyl compounds.

Substance employed, mg	Time of standing, minutes	Iodine consumed, ml 0.009993 *N*	Substance found, mg	Deviation from theory, ‰
		Thiocyanate, ArSeSCN		
None		24.85		
52.96	5	4.37	53.03	+1.3
52.18	5	4.70	52.18	0.0
		Methoxide, $ArSeOCH_3$		
None		24.85		
47.28	15	4.47	47.28	0.0
55.22	15	1.09	55.11	−2.0
45.67	5	5.17	45.64	−0.6
		Ethoxide, $ArSeOC_2H_5$		
None		24.85		
37.94	5	9.42	37.95	+0.2
39.77	5	8.68	39.77	0.0

values, for the 16 analyses listed in the tables, is 0.7 parts per thousand, and the average absolute error is 0.04 mg.

The samples of *o*-nitrobenzeneselenenyl bromide and amide and 2,4-dinitrobenzeneselenenyl bromide, which were available for analysis, gave results which were not in agreement with the theoretical values. It is believed, on the basis of the consistency of the results, that the discrepancies are due to impurities present in the samples, and not to a failure of the analytical method.

Thus, in four separate analyses of 2,4-dinitrobenzeneselenenyl bromide, the results were 0.53, 0.35, 0.33 and 0.44 % too high. The sample used had

Table 2. Iodometric analysis of 2,4-dinitrobenzeneselenenyl compounds.

Substance employed, mg	Time of standing, minutes	Iodine consumed, ml	Substance found, mg	Deviation from theory, ‰
		Thiocyanate, ArSeSCN 0.009993 *N* iodine		
None		24.85		
58.78	5	5.52	58.75	−0.5
36.50	5	12.84	36.50	0.0
		Methoxide, $ArSeOCH_3$ 0.01002 *N* iodine		
None		26.42		
51.85	5	7.77	51.81	−0.7
55.64	5	6.39	55.64	0.0
53.96	5	7.04	53.86	−1.8
		Ethoxide, $ArSeOC_2H_5$ 0.009993 *N* iodine		
None		24.85		
55.37	5	5.84	55.30	−1.2
51.51	5	7.14	51.51	0.0
		Amide, $ArSeNH_2$ 0.01006 *N* iodine		
None		25.06		
53.87	15	4.61	53.92	+0.9
54.78	15	4.24	54.89	+2.0

been recrystallized seven times from chloroform, and melted at 117.5°, as compared with the literature value [7] of 118°. The too high values may be due to impurities of tribromide or hydroxide, which would also react with sodium thiosulphate, and give a lower equivalent weight.

A single analysis of *o*-nitrobenzeneselenenyl bromide, recrystallized once from chloroform, gave a 2 % too low result. Four separate analyses of a sample of *o*-nitrobenzeneselenenyl amide gave results which were 3.6, 3.5, 3.3 and 3.4 % too low. As mentioned earlier, this amide is unstable and could not be obtained in a pure state in spite of repeated recrystallizations.

The present method takes account of compounds only which react with sodium thiosulphate, to give products which are indifferent to iodine. Thus, impurities of diaryl selenides and diselenides, and other compounds which do not react with thiosulphate, will be disclosed by this method of analysis, whereas by ordinary analysis for total selenium content, their presence may not be noticeable.

As a result, it has been observed that many of the selenenyl compounds studied here are more unstable, and more difficult to obtain pure, than believed hitherto.

SOME REARRANGEMENT REACTIONS

In the course of the work, some observations were made on re-esterification reactions of 2,4-dinitrobenzeneselenenyl alkoxides. These compounds, which are esters of the selenenic acid, ArSeOH, react with alcohols:

$$ArSeOC_2H_5 + CH_3OH \rightleftharpoons ArSeOCH_3 + C_2H_5OH$$

Thus, the ethoxide when heated in anhydrous methanol for two hours under reflux, gave practically pure methoxide, as shown by melting point and mixed melting points. The methoxide, treated with anhydrous ethanol under similar conditions, gave a mixture of the two alkoxides. It appears that the above equilibrium may be approached from either side, and that the formation of methoxide from ethoxide takes place more readily than the reverse process. Recrystallization of higher 2,4-dinitrobenzeneselenenyl alkoxides from methanol [11] does therefore not seem advisable.

2,4-Dinitrobenzeneselenenyl amide was found to take part in similar displacements:

$$ArSeOR + NH_3 \rightleftharpoons ArSeNH_2 + ROH$$

The methoxide and ethoxide, in chloroform solutions, on treatment with ammonia gas for two hours, were transformed into the amide. The reverse reactions proceed slowly under anhydrous conditions, but the amide was converted almost completely into the ethoxide when heated in 96 % ethanol under reflux for 90 minutes.

REFERENCES

1. Foss, O. *J. Am. Chem. Soc.* **69** (1947) 2236.
2. Foss, O. *Sjunde nordiska kemistmötet* (1951) Helsingfors, p. 117.
3. Foss, O. *Acta Chem. Scand.* **1** (1947) 307.
4. Foss, O. *Acta Chem. Scand.* **6** (1952) 306.
5. Foss, O. *J. Am. Chem. Soc.* **70** (1948) 421.
6. Behaghel, O. and Seibert, H. *Ber.* **66** (1933) 708.
7. Behaghel, O. and Müller, W. *Ber.* **68** (1935) 1540.
8. From, E. and Martin, K. *Ann.* **401** (1913) 181.
9. Hoggarth, E. and Sexton, W. *J. Chem. Soc.* **1947** 815.
10. Rheinboldt, H. and Perrier, M. *Bull. Soc. chim. France* **17** (1950) 245.
11. Cook, W. S. and Donia, R. A. *J. Am. Chem. Soc.* **73** (1951) 2275.
12. Zincke, T. and Farr, F. *Ann.* **391** (1912) 57.
13. Foss, O. *Kgl. Norske Videnskab. Selskabs Skrifter* **1945** No. 2.

Received May 21, 1954.