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On the Preparation of Some Aliphatic Selenonic Acids

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The potassium and S-benzyl-isothiuronium salts of octyl selenonic acid and decyl selenonic acid have been prepared. The corresponding free selenonic acids are unstable and have not been isolated in a pure state.

In contrast to organic sulfonic acids, their analogues in the selenium series, selenonic acids, $RSeO_3H$, have not been very much studied.[1] This probably depends to a large extent on their pronounced instability, as they are strong oxidizing agents. Besides they are not as easily available as some of the most convenient methods for the preparation of sulfonic acids cannot be applied with advantage to the selenium analogues.[1] Most work on these compounds has been done in the aromatic field, and the only aliphatic selenonic acids so far reported in the literature are the methyl, ethyl, and propyl selenonic acids isolated in the form of their potassium salts,[2] and the — even in dilute solution — very unstable β-aminoethyl selenonic acid.[3] The methane diselenonic acid and ethane-1,2-diselenonic acid reported by Proskauer in 1874 [4] were later considered to have been the corresponding diseleninic acids.[1] In connection with work on aliphatic seleninic acids [5] it was considered of interest to pay some attention to the oxidation products of these acids partly in hope of being able to identify by-products which had been obtained by the oxidation of some diselenides when excess hydrogen peroxide had been used. In this note some observations on the preparation of octyl selenonic acid (III) and decyl selenonic acid (IV) and the corresponding potassium salts (I) and (II) are reported.

The starting materials, octyl seleninic acid and decyl seleninic acid [5] were oxidized in an almost neutral aqueous solution with potassium permanganate.[2]

The oxidant was added slowly, with vigorous stirring, in order to avoid local high concentrations of permanganate, and cooling in ice water. When the reaction was complete the manganese dioxide was filtered off and the

$$3\,C_nH_{2n+1}SeO_2H + 2\,KMnO_4 + KOH \longrightarrow 3\,C_nH_{2n+1}SeO_3K + 2\,MnO_2 + 2\,H_2O$$

I: n = 8

II: n = 10

filtrate carefully neutralized with potassium hydroxide. After evaporation of the water the potassium salts (I) and (II) were obtained as monohydrates. They were recrystallized from absolute alcohol and were in this way obtained in the anhydrous state as glistening flakes. The dry salts seemed to be somewhat hygroscopic.

The purity of (I) and (II) was checked, apart from selenium analyses, by several methods, which indicated the absence of selenite, selenate, and seleninate. Bird and Challenger report that the potassium salt of, *e.g.* propyl selenonic acid decomposes to potassium selenite and the corresponding alcohol on standing,[2] while β-aminoethyl selenonic acid is reported by Pichat *et al.* to decompose into elemental selenium and the corresponding seleninic acid.[3] The presence of potassium selenite or selenate can be tested with barium hydroxide solution.[2] The freshly recrystallized (I) and (II) gave no precipitates with this reagent. However, after the salts had been allowed to stand for some time, this method indicated that some decomposition had taken place. Moreover, the absence of appreciable amounts of seleninates in the freshly recrystallized salts (I) and (II) could be shown in several ways. According to Bird and Challenger [2] aqueous solutions of (I) and (II) gave no reaction when treated with sodium hydrogen sulfite, but when hydrochloric acid was added elemental selenium separated. The corresponding seleninates gave in both cases yellow oils (diselenides). (I) and (II) in acetic acid gave no colour reaction with benzidine, while seleninates immediately give an intense green color turning to red after a short time with this reagent.[6]

Besides, the frequencies of the selenium-oxygen stretching vibrations in the infra-red spectra of the potassium salts of octyl and decyl seleninic acids (in nujol) are found in the 770—830 cm^{-1} region, which is in rather good agreement with the values given by Paetzold *et al.* for the salts of methyl and ethyl seleninic acids.[7] In the region 1300—750 cm^{-1} of the spectra of (I) and (II) (in nujol) there is only one strong and rather broad band at 905 cm^{-1} followed by weak bands or inflexions on its low frequency side at about 865 cm^{-1} and 855 cm^{-1}. This band apparently contains the selenium-oxygen stretching vibrations and its shift to somewhat higher frequencies as compared with the corresponding seleninates is quite analogous to the shift in the same direction of the sulfur-oxygen absorption bands in sulfonates as compared with sulfinates.[8,9] In potassium bromide phase the peak at 905 cm^{-1} seems to be split into two peaks. If the salts (I) and (II) have been allowed to stand for some time the peak at 865 cm^{-1} shows an increased relative intensity. This perhaps indicates a decomposition of the selenonic acid salts.

No derivatives of selenonic acids except a number of metal and ammonium salts are described in the literature.[1] Sulfonic acids often give salts convenient for characterization of the acids with S-benzyl-isothiuronium chloride.[10] With this reagent both (I) and (II) give well-crystallized salts which exhibit rather well defined melting points although accompanied by decomposition. The region for oxygenated selenium groups of the infra-red spectra of these derivatives shows three strong and characteristic peaks between 855 cm^{-1} and 905 cm^{-1} (KBr-phase) while the S-benzyl-isothiuronium salts of the corresponding seleninic acids, prepared for comparison, have one rather strong peak at 800 cm^{-1} (KBr-phase) in the same region. These salts of the seleninic acids do

not crystallize as well as the salts mentioned above and therefore they are not very convenient for the identification of these acids.

Attempts have been made to liberate the octyl selenonic acid (III) and the decyl selenonic acid (IV) from their pure potassium salts. By using a cation exchange resin, the free selenonic acids were obtained in dilute aqueous solution. A potentiometric titration curve showed in both cases the presence of only one acid in the eluate, the equivalent weight of which was in good agreement with the value calculated for the selenonic acid in question. Evaporation of the acid eluates in vacuum at room temperature, however, gave no homogeneous products. The very water soluble white solid residues obtained seemed to contain selenious acid, the respective selenonic acids and probably small amounts of the corresponding seleninic acids and were discolored by some elemental selenium on standing in a desiccator. The pure octyl (III) and decyl selenonic acid (IV) have not yet been isolated from these mixtures. In the region expected for oxygenated selenium groups the infra-red spectra of the products show strong bands at 900 cm^{-1}, 865 cm^{-1} and 695 cm^{-1}, consequently in comparison with seleninic acids a shift to higher frequencies is observed. A rather broad band, similar to that of carboxylic acids, in the 2300—3500 cm^{-1} region indicates strongly hydrogen bonded hydroxyl groups (KBr-phase).

Attempts to determine the oxidation equivalents of the acids (III) and (IV) by iodometric titration were not successful. Though being a strong oxidizing agent, selenic acid is known usually not to oxidize kinetically fast.[11] The same seems to be valid here for the acids (III) and (IV), iodine being liberated over a rather long period. Besides, after a while some selenium is deposited, indicating a side reaction, which makes the oxidation equivalents obtained rather unreliable.

EXPERIMENTAL

The preparation of octyl and decyl seleninic acids has been described earlier.[5] The infra-red spectra were recorded with a Perkin Elmer model 137 spectrophotometer. The potentiometric titrations were performed with a Vibret Laboratory model 46 A pH meter. The cation exchange resins used were Amberlite IR 100 and Dowex 50W—X12. The melting points, all uncorrected, were taken in a Kofler "Heiztisch" microscope. The selenium analyses were carried out according to Fredga.[12]

Potassium salt of decyl selenonic acid (II). 4.57 g powdered decyl seleninic acid was suspended in 70 ml water and 0.34 g potassium hydroxide was added. A solution of 1.90 g potassium permanganate in 100 ml water was dropped over a period of 60 min into this mixture with effective stirring and cooling in ice water. First the oxidation was rapid and the color of the added permanganate disappeared almost immediately, but at the end of this period, when all of the oxidant was added a reddish color persisted. The solution was then carefully neutralized with potassium hydroxide and stirring at room temperature was continued for another 30 min. The color of the potassium permanganate had then disappeared. The manganese dioxide was filtered off from the reaction mixture and after evaporation of the filtrate and drying of the residue in vacuum over sulfuric acid 4.73 g (85 %) of white crystals remained, (drying in air gave the monohydrate of (II)). Recrystallization from absolute alcohol gave white glistening flakes, somewhat hygroscopic. (Found: Se 25.57. Calc. for $C_{10}H_{21}SeO_3K$: Se 25.69).

S-Benzyl-isothiuronium salt of (IV). Equimolar amounts of pure (II) dissolved in water and S-benzyl-isothiuronium chloride in 50 % alcohol were mixed at room temperature. After a short time a precipitate began to form. One recrystallization from 50 % alcohol gave long white needles, m.p. 125.5—126.5° (decomp.). (Found: Se 17.87. Calc. for $C_{18}H_{32}NO_3SSe$: Se 18.08).

Potassium salt of octyl selenonic acid (I). 5.41 g octyl seleninic acid was oxidized with 2.53 g potassium permanganate similarly to the preparation of (II). Here the reaction was more rapid and the oxidant was added over a period of 30 min followed by stirring for another 30 min at room temperature. 6.21 g (92 %) of (I) was obtained, crystallizing from absolute alcohol as white hygroscopic flakes. (Found: Se 28.15. Calc. for $C_8H_{17}KO_3Se$: Se 18.27).

S-Benzyl-isothiuronium salt of (III). This derivative was obtained similarly to that of (*IV*). One recrystallization from 50 % alcohol, followed by one from absolute alcohol gave long white needles, m.p. 142—142.5° (decomp.). (Found: Se 19.28. Calc. for $C_{16}H_{28}NO_3SSe$: Se 19.38).

Decyl selenonic acid (IV). (IV) was liberated from the potassium salt (II) by using an ion exchange resin (Dowex 50W—X12). The eluate was evaporated at room temperature in vacuum over sulfuric acid. A white solid residue (discolored by elemental selenium after two days in a desiccator) was obtained. Most of it melted at 43—45° but a smaller amount persisted till 66°. Treatment of the residue obtained with ether gave a less ether-soluble acid part, the infrared spectrum of which indicated selenious acid. After evaporation of the ether an oil remained which solidified after a while. It had m.p. 41—43° and an equivalent weight of 258.5 (calc. for (IV) 269.2). It did not appear to be homogeneous and when dissolved in water, gave an acid solution and some oily drops on the surface. The acid solution liberated iodine from a potassium iodide solution forming a yellow oil (diselenide) and elemental selenium.

To determine the equivalent weight, the acid (IV) was liberated from a weighed amount of the salt (II), and the eluate immediately titrated potentiometrically. The titration curve indicated the presence of one acid component. (Found: Equiv. wt. 269.6. Calc. for $C_{10}H_{22}O_3Se$: Equiv. wt. 269.2).

Octyl selenonic acid (III). The eluate obtained similarly to that of (IV) gave after evaporation an oil which decomposed, separating elemental selenium, when kept in a desiccator overnight.

The equivalent weight was obtained similarly to that of (IV). The titration curve showed the presence of one acid component. (Found: Equiv. wt. 239.6. Calc. for $C_8H_{18}O_3Se$: Equiv. wt. 241.2).

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Added in proof. Recently the preparation of the potassium salts of ethane-1,2-d selenonic and vinylselenonic acid has been reported [Paetzold, R. *Fortschr. Chem. Forsch.* **5** (1966) 620].

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