

Nucleophilic attack by bromide ions as a first step of conversion of Se(VI) to Se(IV)

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Abstract

Numerous commonly used analytical methods allow only determination of a total amount of selenium in a given sample. Electroanalytical methods as well as those based on hydride generation or on formation of piaszelenol allow only determination of Se(IV). To determine Se(VI) by these procedures, present alone or in mixtures with Se(IV), it is first necessary to convert Se(VI) to Se(IV). Such conversion is effective in the presence of excess of halides in acidic media or by photoreduction. In the often used conversion of Se(VI) in the presence of chlorides or less frequently of that of bromides, it has been assumed that the halide ion acts as a reducing agent. Kinetic studies of conversion of Se(VI) in acidic solutions containing an excess of bromide ions indicated that the rate determining first step of the reaction with Se(VI) is a nucleophilic substitution of the $-\text{OH}_2^+$ group in the protonated form of H_2SeO_4 by bromide ions. For the overall reaction with rate $-\text{d}[\text{Se(VI)}]/\text{d}t = k_1[\text{H}^+][\text{Br}^-]^{1.15}[\text{Se(IV)}]$ the rate constant $1 \times 10^{-3} \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$ was found. The following formation of Se(IV) from the bromo derivative is a fast reaction probably resulting in elimination of HBrO .

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1. Introduction

Selenium is present as trace element in nature. At low level it is essential for fulfilling several important physiological functions, but at higher concentrations it can be toxic. Hence the availability of reliable analytical methods for determination of its concentration is important. As the physiological effects of various forms of selenium differ, determination of all forms in which selenium is present is of interest. In nature selenium can be present in oxidation states +4 and +6 and as organoselenium compounds. The latter are usually converted into inorganic forms during the preparation of the sample. Thus the main analytical problem is the determination of Se(IV) and Se(VI) in a mixture.

Some techniques, like graphite furnace atomic absorption spectrophotometry [1–4], plasma atomic emission spectrophotometry [5], inductively coupled atomic emission spectropho-

tometry or mass spectroscopy [4,6–12] determine only the total amount of the selenium present. To achieve speciation, a separation technique – usually a variant of chromatography – has to be applied prior to the main analytical procedure [4,5,9–12].

Some techniques, such as hydride generation atomic absorption spectrometry [2,3,13–17] or formation of piaszelenol in reaction of selenium (IV) with aromatic diamino compounds, followed by a spectrophotometric [18], fluorometric [19,20] or gas chromatographic [21,22] analysis, allow determination of only selenium in the oxidation state +4.

Similarly, reduction currents obtained by polarography or voltammetry offer information only about the concentration of Se(IV), as species containing Se(VI) are in the available potential range electroinactive. The understanding of the nature of the electrode processes involved is a condition for the successful application of electroanalytical techniques. This condition is fulfilled for the electroreductions of Se(IV), as the role of mercury in these reductions has been reorganized early [23,24]. The role of pH on the electrode process has been reinterpreted [25]. The use of polarography and voltammetry in the determination of Se(IV) has recently been reviewed [26]. Hence

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only some recent applications of the sensitive cathodic stripping voltammetry are quoted here [27–32]. Just one application of electroanalytical procedures, claimed to enable determination of nanomolar quantities of Se(IV) [33–35] will be mentioned here. In the proposed procedure, Se(IV) is reduced by sulfurous acid to Se(0), which with SO_3^{2-} yields an adduct— SeSO_3^{2-} . This species is electrochemically reduced to Se^{2-} . The resulting selenide ion is in the vicinity of the electrode surface reoxidized to SeSO_3^{2-} by iodate in the presence of hydroxylamine at pH 10. This catalyzed reduction of SeSO_3^{2-} is manifested by a high catalytic reduction peak at -0.6 V. The proposed sequence of processes involved has yet to be supported by experimental evidence.

To analyze mixtures containing both Se(IV) and Se(VI) using above-mentioned techniques capable to determine only Se(IV), it is necessary first to determine the concentration of Se(IV) in the analyzed sample, then convert Se(VI) quantitatively to Se(IV), determine the sum of concentrations of Se(IV) and Se(VI) and to obtain the concentration of Se(VI) from the difference of results of the two above described determinations.

The choice of the reagent enabling a complete conversion of Se(VI) and Se(IV) is limited by the following constrains.

Commonly used reducing agents, such as hydrazine and hydroxylamine reduce Se(VI) to Se(0) [36]. Formation of Se(0) has been observed also in the presence of KI and H_2S [19]. Sodium borohydride reduces Se(VI) and Se(IV) all the way to Se^{2-} [36,37]. Sulfur dioxide does not reduce Se(VI) but reduces Se(IV) to Se(0) [36]. Addition of hydrogen peroxide results in a partial reduction of Se(VI) to Se(IV) [36].

Attempts have been made to convert Se(VI) into Se(IV) using irradiation of the sample using UV-light from a mercury lamp. This has been carried out both as a homogeneous and a heterogeneous process. In the homogeneous process a solution of Se(VI) containing 0.03% hydrogen peroxide and 0.1 M HCl was irradiated for about 1 h. (Significantly, when the same approach was carried out using 0.1 M H_2SO_4 or 0.1 M HClO_4 no reduction was observed.) To achieve a 90% conversion, addition of glucose or maleic acid was necessary. In the presence of other organic compounds lower conversion was observed. It was concluded [29] that the “irradiation procedure is empirical and its physico-chemical rationale is unknown.”

In other experiments in homogeneous solution, in the absence of glucose or hydrogen peroxide, about 100% conversion of Se(VI) into Se(IV) has been reported [27], when the solution containing chloride ions from investigated seawater was irradiated for 4 h [27]. Alternatively, irradiation at pH 11.0 for 1 h was proposed [38].

Photoreduction of Se(VI) was also attempted in heterogeneous systems, particularly in the presence of TiO_2 or silver loaded TiO_2 in the presence of formic acid [39,40]. In the first step the reduction yielded only Se(0), but when Se(VI) was exhausted, some reduction of Se(0) to Se(-II) took place. Reduction of Se(VI) has also been observed in the presence of enzymes [41] and bacteria [42–46], but this reaction has not been used for analysis.

The conversion of Se(VI) to Se(IV) can be achieved in solutions acidified by hydrochloric or perchloric acid in the

presence of varying concentration of chloride ions at temperatures between 90°C and 100°C over varying periods of time [28,32,34–36,47–49]. The separate roles of acidity and chloride ions on the degree of conversion and the optimum time-period were, nevertheless, not clearly established. Thus, for example, the 100% conversion in 6 M HCl took at 90°C several hours to establish [36]. Alternatively, such conversion was reported to be achieved in 5.8 KBr at 100°C [15] or in 0.1 M KBr in 1.3 M HCl at either 90°C or at boiling point under reflux [20].

In all these investigations it was assumed that the halide acts as a reducing agent. Attempts to offer an interpretation based on comparison of standard potentials (sometimes using doubtful data [20]) are doubtful, as their use assumes a reversibility of the oxidation–reduction process. The time-periods and temperature needed for establishing the conversion strongly indicated that the processes involved are controlled by kinetics rather than thermodynamics. The essential consequence of a simple oxidation–reduction process would be formation of equivalent amounts of molecular Cl_2 or Br_2 . No such observation has been reported, even when the reaction mixture was kept under reflux.

In this communication we propose that the initial step of the conversion of Se(VI) to Se(IV) in the presence of halides is a nucleophilic substitution by a protonated OH groups by the halide in an acid catalyzed reaction.

2. Experimental

2.1. Apparatus

Current–voltage curves were recorded using a PAR Model 174A Polarographic Analyzer with drop-time control. The capillary electrode used had natural by drop-time 2 to 3 s with out-flow velocity of 2.9 mg s^{-1} at mercury pressure used. A Kalousek electrolytic cell in which the KCl solution was replaced by 4 M NaCl to prevent formation of KClO , with an CE reference electrode, separated by a liquid junction, was used in a three-electrode configuration. The counter-electrode consisted of a Pt-wire.

DC polarograms were recorded with a Linseis LY 1600 X–Y recorder (Selt, Germany) using controlled drop-time of 2 s at a scan rate of 5 mV/s, DP polarograms with $t_1 = 1$ s at the same scan rate and pulse amplitude of 50 mV.

2.2. Reagents

Perchloric, hydrochloric, sulfuric acid and sodium bromide were analytical reagent grade. 0.1 M standard solution of Se(VI) was prepared by dissolving SeO_2 in hot water. Dilute solutions of Se(IV) were prepared fresh daily. Solute of 4 M NaClO_4 was prepared in situ by titrating HClO_4 by NaOH.

2.3. Procedures

2.3.1. Conversion yield

In previous studies the conversion of Se(VI) to Se(IV) was achieved in solutions containing 4–6 M HCl after boiling for 15–60 min [28,30,34–36]. Japanese authors [20] carried out the

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