Mass Spectral Investigations on Benzeneseleninic Acid †

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The mass spectra of benzeneseleninic acid and of diphenyl diselenide have been examined and a full analysis is reported. The fragmentation patterns and the fragment ions are discussed. A molecular-ion peak was not observed for benzeneseleninic acid; instead the ion with highest mass number appeared in a multiplet, with the most intense peak at *m/e* 314, having a general shape typical of the presence of two selenium atoms and corresponding to the diphenyl diselenide (C_6H_5–Se–Se–C_6H_5) ion.

THIS work is part of a study on the chemical and physical behaviour of benzeneseleninic acid. In previous papers [1,2] we reported the dissociation equilibrium constants of several *para*- and *meta*-substituted benzeneseleninic acids in aqueous media, at different temperatures and at different ionic strengths. Analytical, kinetic, and i.r. spectral aspects of these derivatives have also been studied.[3-5]

The benzeneseleninato-ion is quite a peculiar ligand; it can behave as a unidentate ligand with the metal ion linked directly to the selenium or to an oxygen atom (seleninato-*Se* or -*O*) or as a bidentate ligand, either intra- or inter-molecularly, *via* the two oxygen atoms (seleninato-*OO'*) or *via* the selenium atom and one of the oxygens (seleninato-*SeO*). Each of these types of co-ordination, the chemical reactivity, and linkage isomers of the co-ordination compounds towards *N*-donor ligands have been observed in our studies and reported in previous papers.[6-16]

The investigation reported here on the mass spectra of benzeneseleninic acid and of diphenyl diselenide is the first step of a study of the *para*- and *meta*-substituted derivatives and their *d*- and *p*-block metal complexes. This paper describes both the basic fragmentation processes and the complex reorganisation which occurs in the spectrum of the acid.

RESULTS AND DISCUSSION

Benzeneseleninic acid gives rise to fragmentations of a complex nature, however, the presence of the selenium atom, having many stable isotopes (^{74}Se 0.87%, ^{76}Se 9.02%, ^{77}Se 7.58%, ^{78}Se 23.52%, ^{80}Se 49.82%, and ^{82}Se 9.19%),[17] provides a useful aid in the assignment of the peaks. All the reported *m/e* values refer to multiplets when selenium is present but the figure given is that of the most abundant isotope ^{80}Se.

A basic feature noted at the beginning of this work, when the mass spectrum of C_6H_5SeOOH was recorded, was the absence of a molecular-ion peak, expected as a multiplet with the most intense peak at *m/e* 190. The ion with the highest mass number observed is part of a multiplet with the most intense peak at *m/e* 314, having a general shape typical of the presence of two selenium atoms. The calculations carried out using the natural isotopic abundance were in very good agreement with the bar diagram intensities; this ion corresponds to diphenyl diselenide, C_6H_5–Se–Se–C_6H_5, whose mass is 314.

Starting from these results we have used the diphenyl diselenide mass spectrum, in which the parent ion is at *m/e* 314, as a basis for further studies. The mass spectrum of C_6H_5–Se–Se–C_6H_5 and the mode of decomposition postulated are shown in Figure 1. Two principal fragmentation patterns can be suggested for this compound.

(*i*) A homolytic division of the Se–Se bond leading to the formation of the ion $[C_6H_5Se]^+$ (*m/e* 157), the multiplet of which shows intensities which are characteristic of the presence of only one selenium atom. From this ion we obtain, after loss of selenium atom, the peak at *m/e* 77, which is the base peak and is attributed to $[C_6H_5]^+$. It is worth noting that the multiplicity of peaks typical of the presence of selenium atoms is absent in this last ion; we also observe peaks at *m/e* 51 and 50, which are typical of phenyl fragmentation.

The singlets at *m/e* 65 and 39 and the peaks at *m/e* 51 and 50 could derive directly from the ion $[C_6H_5Se]^+$ (*m/e* 157) through loss of a CSe group; this fact is in agreement with the loss of CO and CS groups observed in the fragmentation processes of the analogous $[C_6H_5O]^+$ and $[C_6H_5S]^+$ ions.[18,19]

The peak at *m/e* 117 is of doubtful interpretation but, having a multiplet shape characteristic of the presence of one selenium atom only, it could be tentatively assigned to an ion of the type $[C_3HSe]^{\cdot +}$ arising from the peak at 157.

(*ii*) In the second fragmentation process the first step is the loss of a selenium atom giving the ion at *m/e* 234, whose multiplet intensity is diagnostic of the presence of only one selenium atom. By losing a second selenium atom, a single peak at *m/e* 154, due to the diphenyl ion, is obtained.

Obviously it is possible that there is an interaction between the two postulated pathways resulting in the loss of a phenyl radical, Figure 1.

With reference to benzeneseleninic acid, from the above considerations regarding the absence of a molecular-ion peak and the presence of a peak corresponding exactly to the mass of diphenyl diselenide, it is clear that during the experiment a reaction must take place,

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† The results of this work were presented at the World Spectroscopy Conference, Lisbon, Portugal, 2-3 July, 1979.

accompanied by reduction of the selenium. Hence, it must be assumed that at the moment of introduction of the sample into the ion source, maintained at a pressure equal to *ca.* 10^{-6} mmHg,* a redox condensation of type (1) takes place. The diphenyl diselenide then undergoes

$$2C_6H_5SeOOH \longrightarrow C_6H_5\text{-}Se\text{-}Se\text{-}C_6H_5 + \tfrac{3}{2}O_2 + H_2O \quad (1)$$

the ionization (2).

$$C_6H_5\text{-}Se\text{-}Se\text{-}C_6H_5 + e^- \longrightarrow [C_6H_5\text{-}Se\text{-}Se\text{-}C_6H_5]^{\cdot +} + 2e^- \quad (2)$$

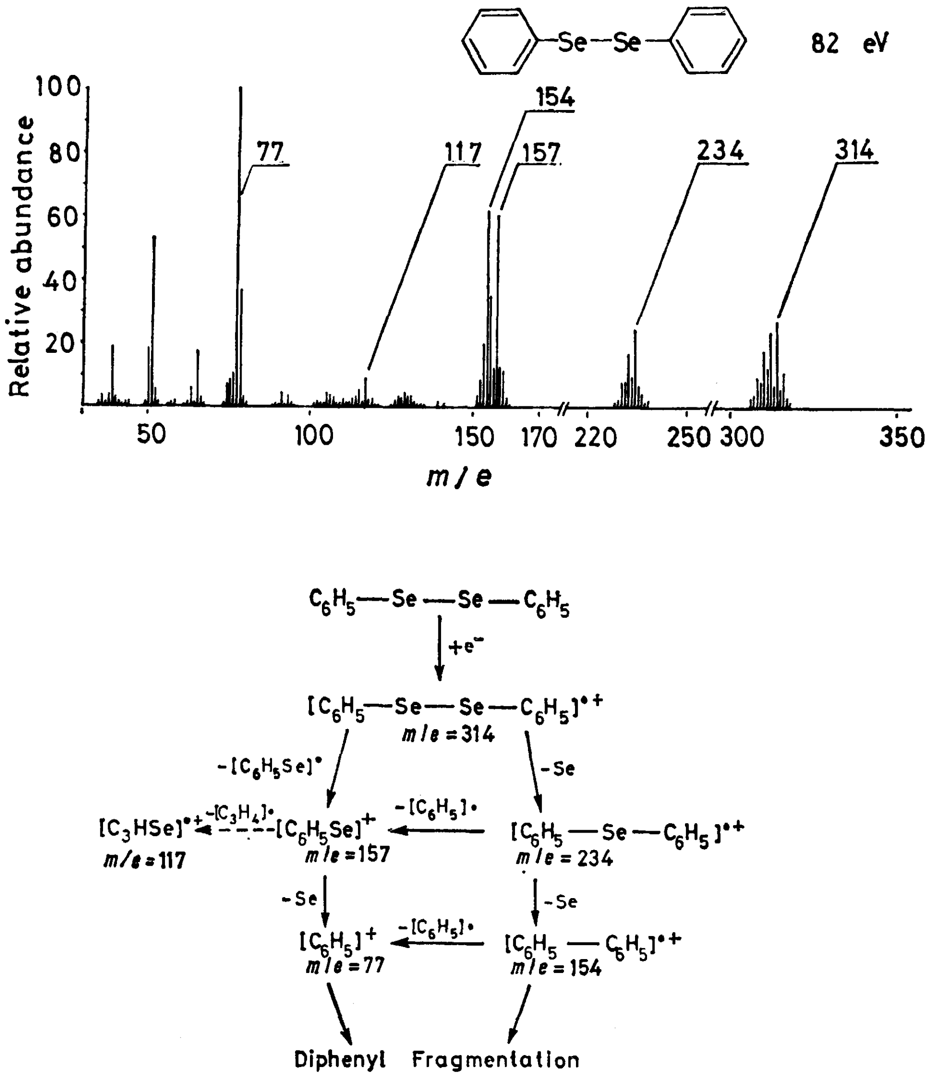

FIGURE 1 Mass spectrum and decomposition pathway of diphenyl diselenide

A confirmation of this hypothesis comes from the examination of two spectra of benzeneseleninic acid, recorded at 82 and 40 eV respectively, Figure 2. The comparison shows that the multiplet having the most intense peak at *m/e* 314 increases in intensity from 10.8 to 35.3% with the decrease in energy. This proves that it is almost certainly the diselenide moiety that undergoes the ionization. Furthermore, the base peak changes from 157 to 77 on going from one set of experimental conditions to the other.

An alternative ion–molecule interaction of the type (3), leading to the same experimental result, must be considered very unlikely at a source pressure of 10^{-6} mmHg.

$$[C_6H_5SeOOH]^{\cdot +} + C_6H_5SeOOH \longrightarrow [C_6H_5\text{-}Se\text{-}Se\text{-}C_6H_5]^{\cdot +} + \tfrac{3}{2}O_2 + H_2O \quad (3)$$

The fragmentation process of benzeneseleninic acid starts from the peak at *m/e* 314, attributed to the diphenyl diselenide ion, present in the spectrum as a multiplet typical of the presence of two selenium atoms, and continues *via* the same mechanism as diphenyl diselenide, following the two principal pathways discussed above (Figure 1).

The presence in the spectrum of many other peaks,

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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

very low in intensity, leads us to propose an alternative non-redox condensation (4) followed by the ionization (5).

$$2C_6H_5SeOOH \longrightarrow C_6H_5\text{-}Se(=O)\text{-}C_6H_5 + SeO_2 + H_2O \quad (4)$$

$$C_6H_5\text{-}Se(=O)\text{-}C_6H_5 + e^- \longrightarrow [C_6H_5\text{-}Se(=O)\text{-}C_6H_5]^{\cdot +} + 2e^- \quad (5)$$

In this way we can explain the presence of a group of peaks typical of just one selenium atom, having the most intense peak at *m/e* 250, and attributed to the ion $[(C_6H_5)_2Se{=}O]^{\cdot +}$. From here another fragmentation path can proceed; this route is certainly less significant than the one discussed previously, but it is the only one which provides an explanation for the peaks with a multiplet structure at *m/e* 173 and 174, attributed to the $[C_6H_5SeO]^+$ and $[C_6H_5SeOH]^+$ ions respectively, and the singlet at *m/e* 76, due to $[C_6H_4]^+$. The peaks at *m/e* 174 and 173 are present as multiplets, each typical of the presence of one selenium atom.

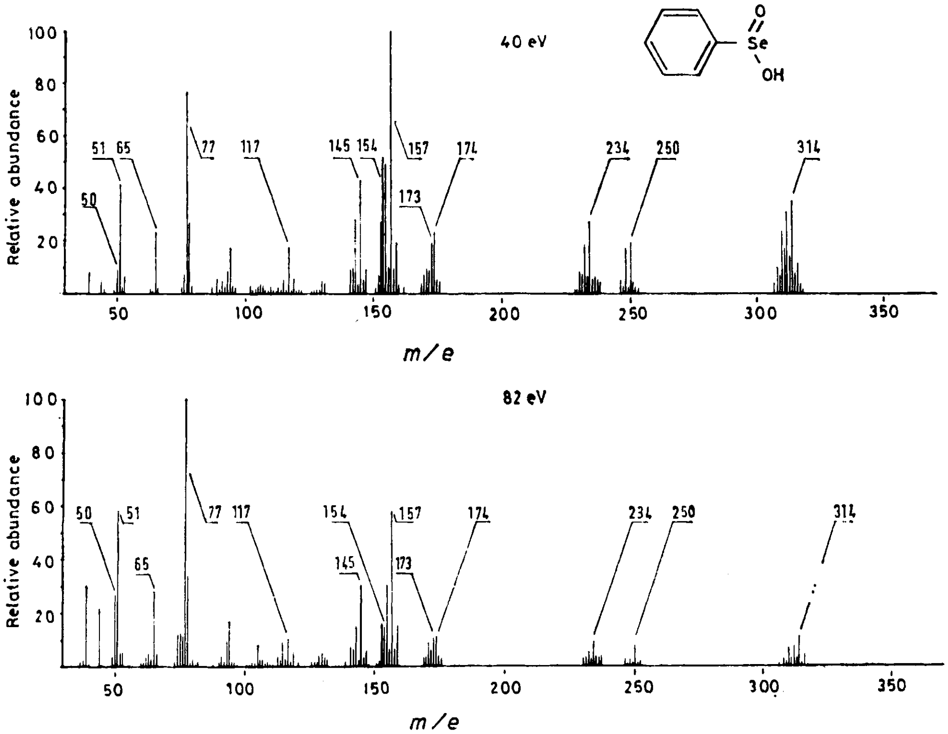

FIGURE 2 Mass spectra of C_6H_5SeOOH recorded at 40 and 82 eV

EXPERIMENTAL

Preparation of the Compounds.—Benzeneseleninic acid and diphenyl diselenide were prepared according to reported methods,[2,3,20] to which small modifications were introduced in order to improve the yields. The compounds were analyzed by a Perkin-Elmer 240 C,H,N, analyzer and their purity was evaluated by a variety of methods: melting point, i.r. spectra in the 35—4 000 cm^{-1} region with a Perkin-Elmer 180 spectrophotometer and, in the case of benzeneseleninic acid, titration with KI in acidic medium according to reaction (6), potentiometric titrations in a stream of nitrogen with a 0.1 mol dm^{-3} carbonate-free solution of Na[OH] using a Polymetron 42B potentiometer equipped with a glass electrode, and conductivity titrations (WTW LBR type conductivity bridge) in 2-methoxyethanol as solvent using 0.1 mol dm^{-3} diphenylguanidine as titrant.[21]

$$2C_6H_5SeOOH + 6KI + 3H_2SO_4 \longrightarrow C_6H_5\text{-}Se\text{-}Se\text{-}C_6H_5 + 3I_2 + 3K_2[SO_4] + 4H_2O \quad (6)$$

Mass Spectra Experiments.—The mass spectra were recorded on a Varian MAT 112 double-focusing mass spectrometer equipped with a direct inlet system and operating at 82 and 40 eV; all the spectra were measured at the lowest possible temperatures. Isotopic pattern calculations were performed when necessary. The spectra normalization was carried out with a Varian 620 L computer and the recorded values in the spectra are the mean values of at least five runs.

[9/1209 *Received*, 31*st July*, 1979]

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