

## Pulse Radiolysis of Selenium Containing Compounds: Selenomethionine

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The pulse radiolysis of aqueous solutions of selenomethionine has been studied under both neutral and acid conditions and the transient optical absorption spectra have been observed. The reactivities of both  $e_{aq}^-$  and OH radicals have been measured as well as the formation and the decay kinetics of the transient species.

We have carried out in the past a study on the radiation effects on selenium-containing compounds, such as selenourea<sup>1</sup> and selenocystine<sup>2</sup>, where the selenium atom is present in different types of structures. This paper deals with some preliminary results on the pulse radiolysis of selenomethionine, an amino acid containing the C-Se-C bond. Selenomethionine is an interesting amino acid for its high biological activity<sup>3</sup> and for its radioprotective properties<sup>4</sup>.

DL-selenomethionine, supplied by Sigma, was used without further purification. All solutions were made up in triply distilled water. The pulse radiolysis experiments have been carried out using the 2 MeV electron accelerator Febetron 705 (Field Emission Corp.) and the apparatus has been described previously<sup>2</sup>.

The Figure represents the spectra of  $5 \cdot 10^{-4}$  M selenomethionine solutions under different experimental conditions. In deaerated solution, at neutral pH, a strong absorption maximum at 380 nm was observed. This absorption was doubled when the solution was saturated with  $N_2O$ , which converts  $e_{aq}^-$  into OH radicals. This indicates that the transient absorption was due to OH radical attack on selenomethionine. In  $N_2O$  saturated solution and in the presence of *tert*-butanol, which scavenges OH radicals leaving only H atoms, the absorption was negligible. In acid solution, the absorption maximum shifts to longer wavelengths (480 nm). This absorption was strongly decreased in the presence of *tert*-butanol, suggesting that the bulk of the absorption was also due to the reaction of OH radicals with selenomethionine. In neutral solution, the rate of formation of the species absorbing at 380 nm was measured from the build-up and a value of about  $1 \cdot 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$  was obtained for the bimolecular rate constant. From competitive experiments, using  $CNS^-$  as competing solute<sup>5</sup> a rate constant  $k$  (OH + selenomethionine) =  $1.3 \cdot 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$  was found, in agreement with the value obtained directly. The decay kinetics of this transient species are complex since the decay is first-order at low irradiation doses (< 500 rads) but mixed order at higher doses. The spectra remained unchanged in shape at the different irradiation doses and at various times after the electron pulse. The rate constant of the first-order decay, which is independent of selenomethionine concentration, is equal to  $5.7 \cdot 10^8 \text{ sec}^{-1}$ . If we assume that at high doses the disappearance of the 380 nm absorption occurs by concurrent first and second-order reactions, the decay curve may be analyzed by an approximate kinetics method<sup>6</sup>. The rate constant for the first-order reaction, calculated in this way, is in fairly good agreement with the value obtained at low doses, where the second-order process is negligible, suggesting that the previous assumption was correct. At higher doses, the second-order component of the decay has a rate constant of about  $4 \cdot 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ . The reaction of  $e_{aq}^-$  is fast ( $k = 1.8 \cdot 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ ), but the product has no significant absorption in the visible and ultraviolet region.

These preliminary data show high reactivity of selenomethionine with both OH radicals and  $e_{aq}^-$ , as has been observed for other aliphatic amino acids containing selenium<sup>2</sup> and sulphur<sup>7</sup>. Further, the intense absorption produced by reaction of selenomethionine with OH radicals is not observed for the common aliphatic amino acids. It is difficult to identify the radical absorbing at 380 nm but definitively the unpaired electron is not on a carbon atom. We believe that the OH attack occurs at the selenium atoms. The resulting radical decay by two alternative ways: The exponential decay observed at low doses may be due to a unimolecular decomposition or to an internal rearrangement; the bimolecular reaction observed at high doses, probably

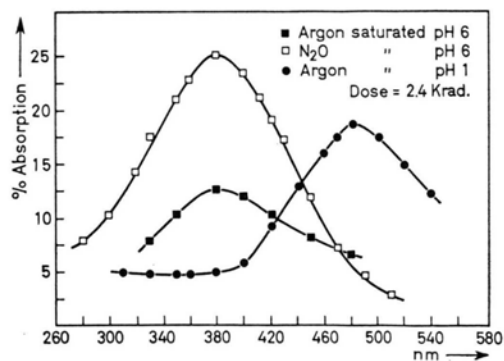


Figure. Transient spectra in  $5 \cdot 10^{-4}$  M selenomethionine aqueous solutions. Path cell = 2 cm.

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involves neutral radicals since the decay kinetics seem to be not affected by changes in ionic strength. Steady-state irradiation of selenomethionine has shown that the molecule is decomposed mainly by OH radical attack meanwhile  $e_{aq}^-$  are scavenged by the selenium atoms without any degradation of the molecule<sup>8</sup>. Moreover, the main radiolysis reactions are the elimination of  $-SeCH_3$  and  $-CH_3$  groups with subsequent formation of recombination products. On the contrary, in the case of methionine, the most important radiolysis process is the oxidation of sulphur to the highest valence state, leaving the skeleton of the molecule unaffected<sup>9</sup>. IR spectroscopy of selenomethionine and methionine<sup>10</sup> supports their different radiation behaviour. It has been shown that the Se-C bond is less stable than the S-C bond. This can in part explain the presence of recombination products in the steady-state degradation of selenomethionine. The pulse radiolysis data show that the early radicals formed from

selenomethionine are relatively long-lived and therefore they can easily react together to give the final products. Preliminary results by van HEMMEN and ADAMS<sup>11</sup> showed, by pulse radiolysis, that an intense absorption at around 400 nm is formed by OH attack on methionine. This species decays rapidly with a first-order kinetics to give a longer-lived absorption at shorter wavelengths. These species have not yet been identified. The present results show that, as is observed for other sulphur and selenium compounds, substitution of sulphur by selenium leads to a different response to radiation, but further pulse radiolysis investigations on the nature of radical species derived from selenomethionine and methionine are necessary to explain these differences.

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