The Squaric Acid Derivatives $C_8O_4S_2$ and $C_8O_4Se_2$ – Crystal Structures, Explosive Thermal Behavior and the Preparation of Carbon Suboxide Selenide OC_3Se by Flash Vacuum Pyrolysis

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2,7-Diselenatricyclo[6.2.0.0$^{3.6}$]deca-1,3-diene-4,5,9,10-tetraone, $C_8O_4Se_2$, was prepared from 1,2-diselenosquarate and squaric acid dichloride. Its crystal structure and the structure of the already known sulfur analogue $C_8O_4S_2$ were determined ($C_8O_4S_2$: orthorhombic, $Pca2_1$, $a = 1413.64(2)$, $b = 599.850(9)$, $c = 968.8(1)$ pm; $C_8O_4Se_2$: orthorhombic, $Pnnm$, $a = 415.46(2)$, $b = 894.29(5)$, $c = 1160.14(7)$ pm). The structures are not isotypic and show a different packing of the molecules whose symmetry deviate only slightly from D_{2h}. In the four-membered C_4 rings the C–C bonds represent one single bond, one double bond and two slightly shortened single bonds. The C_4 rings are thus to be considered as cyclobutene-dione fragments. The vigorous exothermic decomposition of the compounds that occurs on heating to 220 to 240 °C shows that both are energetic materials. The explosions are accompanied by a heat evolution of −192 kJ/mol for $C_8O_4S_2$ and −224 kJ/mol for $C_8O_4Se_2$. Performing the decomposition of $C_8O_4S_2$ in a closed autoclave leaves a residue of the composition "C_6S" which was examined by transmission electron microscopy techniques and shown to consist mainly of amorphous carbon. This thermal behaviour is limiting the utilization of $C_8O_4S_2$ and $C_8O_4Se_2$ as precursors for the syntheses of OC_3S and the yet unknown OC_3Se *via* FVP. The formation of OC_3S could be proven by the reaction of the trapped, slightly yellow product (evaporation at 200 °C, pyrolysis at 500 °C, trapping at −196 °C) with aniline which yielded thiomalonic acid dianilide, of which the crystal structure was determined (monoclinic, $C2/c$, $a = 2814.8(16)$, $b = 1201.7(8)$, $c = 809.2(4)$ pm, $\beta = 91.88(4)°$, $V = 2736(3) \cdot 10^6$ pm^3). The mass spectrum of $C_8O_4Se_2$ shows the strongest signal for OC_3Se^+, and FVP experiments (evaporation at 220 °C, pyrolysis at 650 °C, trapping at −75 °C) yielded small amounts of a bright yellow material which rapidly converted into a black polymer.

Key words: Squaric Acid Derivatives, Energetic Materials, Amorphous Carbon, Carbon Suboxide Selenide, Flash Vacuum Pyrolysis