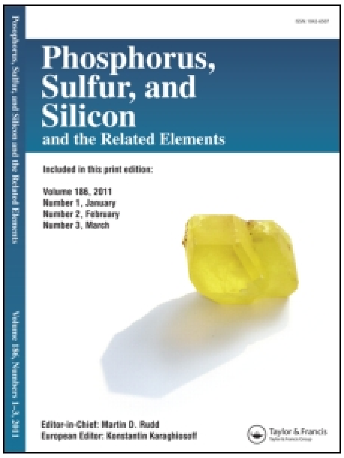

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Preparation, Characterization, and Degradation of Environmentally Important Mercury(II)Organylthiolates

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Mercury and its compounds are known to have a significant environmental impact.[1] Mobilized mercury is highly toxic to many organisms, mainly because of its high affinity to compounds with sulphur containing functional groups, such as thiols and disulfides. Therefore, it is of great importance to better understand the chemistry of mercury, laying emphasis on mechanisms of formation and degradation of compounds containing sulphur, such as mercuryorganylthiolates.

The formation and the degradation of the title compounds as outlined in Eq. 1 could be revealed to occur in a very narrow temperature window.[2] Similar reactions, however photochemically initiated, have been published by EMÉLEUS et al..[3]

$$\mathrm{Hg} + \mathrm{RSSR} \underset{\text{high T}}{\overset{\text{low T}}{\rightleftharpoons}} \mathrm{RSHgSR} \qquad (1)$$

The reason for this behaviour must be seen in the narrow temperature gap between the melting point of most of these compounds and the onset of their decomposition. Thermochemical investigations of a series of these compounds ($R = CH_3 - C_{12}H_{25}$) have shown that all compounds with the exception of the methylthiolate parent derivative have a distinct melting point at approximately 75 °C. The parent compound has no melting point. Complete decomposition of the majority of these compounds in the solid state is achieved within a temperature range of approximately 80 °C. Decomposition starts near 100 °C with a maximum at about 150 °C to 170 °C, whereas the decomposition of the methylthiolate derivative starts at approximatly 150 °C with a reaction maximum at 190 °C. That is the reason why the formation of those mercury(II)alkylthiolates containing longer chained alkyl groups proceeds at low temperature, not much higher than ambient temperature, whereas the mercury(II)dimethylthiolate is even formed at temperatures as high as 100 °C. In solution the thermal decomposition of these compounds results in the formation of mercury and the corresponding dialkyl disulfide,[4] whereas in the solid state mercury sulfide and the corresponding dialkyl sulfide are formed in addition, as exemplified in Eqs. 2 and 3:

$$Hg(SR)_2 \xrightarrow{\text{T, solution}} Hg + RSSR \qquad (2)$$

$$Hg(SR)_2 \xrightarrow{\text{T, solid}} Hg + HgS + RSSR + RSR \qquad (3)$$

The influence of iron and ironsulfides significantly enhances the decomposition of the title compounds.

Mercury(II)organylthiolates easily exchange thiolate groups with organic thiols and organic disulfides according to Eqs. 4 and 5. The exchange reaction proceeds already at room temperature. Similar reactions are known from methylmercury thiolates.[5]

$$Hg(SR)_2 + 2\,R'SH \rightleftharpoons Hg(SR')_2 + 2\,RSH \qquad (4)$$

$$Hg(SR)_2 + R'SSR' \rightleftharpoons Hg(SR')_2 + RSSR \qquad (5)$$

In solution the equilibria of these reactions are shifted to the mercury diorganylthiolate containing the thiolate group of that thiol or disulfide which is employed in excess. These exchange reactions are of particular interest in ecological systems.

Moreover, this particular reaction has a significant impact on the equilibration reaction of two different disulfides as shown in Eq. 6. In the presence of mercury(II)dithiolates the equilibrium is achieved within a few days, whereas the exchange reaction is very slow in their absence, if it proceeds at all.

$$RSSR + R'SSR' \overset{Hg(SR)_2}{\rightleftharpoons} 2\,RSSR' \qquad (6)$$

Reactions (1) to (6) compete with each other; at high temperature decomposition reactions predominate, whereas at low temperature formation of mercury(II)thiolates and exchange reactions are in equilibrium. Thus, it becomes obvious that different pathways of mobilization of mercury into the environment are possible.

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