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An Electron Spin Resonance Study of Metal Organic Radical Ion-pair Exchanges Involving Methylmercury

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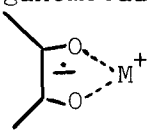
Inorganic cations and metal complexes play vital roles in biological systems but their concentrations must be regulated, either by mechanisms existing in the system or by externally imposed controls. One of the external controls is to employ chelating agents which can seek out excessive and thus toxic metal to bind and excrete them as complexes. The chelating agents may initially carry essential metals such as Na or K, and deliver them to tissues that require them. Methylmercury poisoning has generally been recognized as an environmental health harzard. Toxicology studies (MACGREGOR and CLARKSON 1974) suggest that essentially all the methylmercury in the blood and tissues of exposed animals and humans is complexed by sulfhydryl groups of cystein-containing peptides and proteins. Despite their thermodynamic stability, these complexes are known to be labile and exchange among multitude of chelating groups they encounter. Thus, chemotherapeutic agent such as N-acetyl-D,L-penicillamine has been used to extract methylmercury from the red blood cell and tissues (AASETH 1976). The present study explores the use of electron spin resonance method to study the exchange reactions between methylmercury and alkali metal in 'complexed' ion-pairs.

The chemical reactivity of 9,10-phenanthroquinone (PQ) to form alkali radical ion-pairs and organometal spin adducts has been demonstrated (MOCHIDA et al 1978). Similar to other alkali radical ion-pairs and triple ions of a series of dicarbonyl compounds (CHEN and WAN 1978), exchanges of the alkali metal cations either within tha alkali family or with other heavy metalorganics such as Sn, Pb, and Hg, are very specific and highly efficient. The alkali-PQ radical ion-pairs and the PQ-organometal adducts have a general structure



which is consistent with the electron spin resonance analysis. The experimental method of generating metal ion-pairs has been previously described. The e.s.r. spectra were recorded on a Bruker 420 spectrometer with 100 kHz modulation. Magnetic field and microwave frequency measurements were made

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with a Bruker nmr oscillator and a Hewlett Packard frequency counter, respectively.

In pure tetrahydrofuran solvent (THF) with a trace of methylmercury chloride, ion-exchange occurs

$$K^+PQ^{\cdot-} + (CH_3)HgCl \longrightarrow (CH_3)Hg^{\cdot}PQ + KCl$$

and the e.s.r. spectrum of the new adduct $(CH_3)Hg^{\cdot}PQ$ is observed. The identity of the mercury adduct was confirmed by generating the species in a different manner and with a number of organomercury compounds, including the diphenylmercury and the dibenzylmercury. All of these mercury adducts have a very unique low g-factor, 2.0002 and hyperfine splittings from the isotope Hg-199 (16.86%, I=½) can also be resolved in the phenylmercury adduct. For comparison we have prepared the $(CH_3)_3Pb$-PQ adduct which has a 'normal' g-factor of 2.004.[3] The g-factor for the $(CH_3)_3Sn$-PQ adduct is also 2.004.

The K^+/CH_3Hg exchange is not as rapid as the Pb and the Sn systems.[3] However, the exchange will proceed to completion within a few hours. When water is added to the solution (5:3 vol mixture), the exchange reaction appears to proceed faster but some of the methylmercury adducts will be in equilibrium with their dissociated forms. The concentration of water appears to be less important to the equilibrium. Such exchange reaction would therefore be expected to proceed in biological systems.

Because of the specially low g-factor of the methylmercury-PQ adducts, e.s.r. method is a valuable tool to identify the presence of traces of methylmercury even in the presence of other heavy metals. Quantitative analysis can be made by careful standardization and calibration procedures involving double integration of the spectra. Since initial and milder symptoms of methylmercury poisoning are similar to symptoms arising from other more usual phenomena, it is desirable to develop a simple and convenient method for early detection of methylmercury blood concentrations. The specific features of the methylmercury-PQ adduct afford such a suitable means.

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