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## Immobilization of Fission Iodine by Reaction with a Fullerene Containing Carbon Compound and Insoluble Natural Organic Matrix: Quaterly Report January-March 2006

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## Quarterly Report for January, February and March 2006

**Date:** Reported on April 17, 2006

**Site:** UNLV Chemistry Department

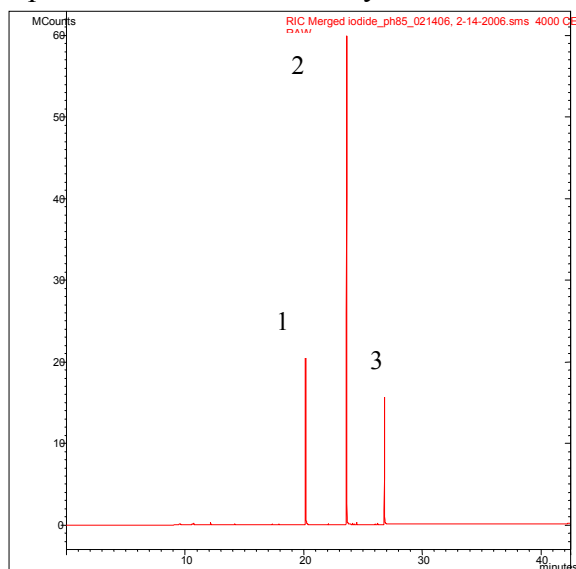
**Project Title:** Immobilization of Fission Iodine by Reaction with a Fullerene Containing Carbon Compound and Insoluble Natural Organic Matrix - S. Steinberg, PI.

**Area:** Transmutation, TRP Program

Project Highlights:

- Established that iodide can be oxidized by  $\text{MnO}_2$  to  $\text{I}_2$  at pHs of 4-8 and moderate temperature.
- Demonstrated that p-hydroxybenzoic acid can be iodinated by  $\text{MnO}_2$  and KI at pHs of 2-8.
- Established that humic acids can be iodinated by  $\text{MnO}_2$  and iodide at room temperature in pH range of 4-8.

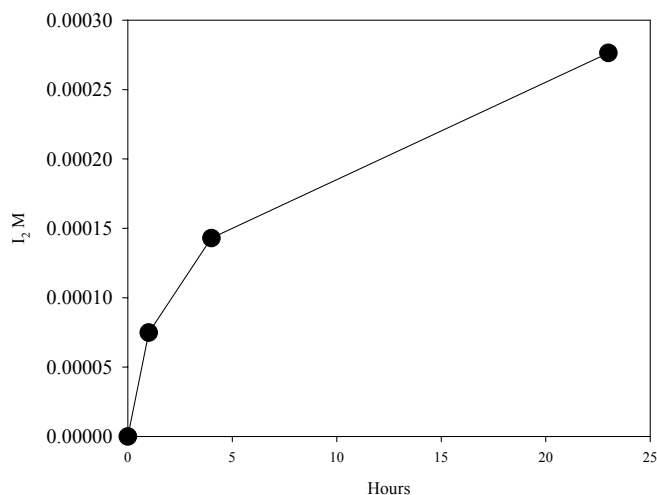
Manganese oxide minerals (Mn(III) or Mn(IV)) were demonstrated as also being capable of oxidizing iodide under mild conditions (pH 4-8) at  $\sim 25^\circ\text{C}$ . For example, treatment of a 0.02M solution of p-hydroxybenzoic acid (PHBA) with 0.1M KI (pH 8.5, 0.1 M  $\text{NaHCO}_3$  buffer) resulted in the formation of 3-iodo-p-hydroxybenzoate and 3,5-diiodo-p-hydroxybenzoate. Both products were identified by GC/MS of the silanated derivatives.



**Figure 1:** The chromatogram from an experiment where 0.1M KI (pH 8.5) was allowed to react with p-hydroxybenzoic acid in the presence of  $\text{MnO}_2$  (Birnessite). The three peaks were identified (in order of retention time) p-hydroxybenzoic acid (1), 3-iodo-p-hydroxybenzoic acid (2) and 3,5-diiodo-p-hydroxybenzoic acid (3).

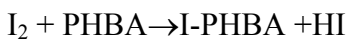
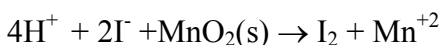
The formation of iodine (as  $I_3^-$ ) was also confirmed in several different buffered solutions of potassium iodide that have been exposed to manganese oxide minerals. From these preliminary results it is clear that oxidation of iodide can occur at moderate pH. An example of this is shown in Figure 2.

#### Formation of Iodine at pH 8.5



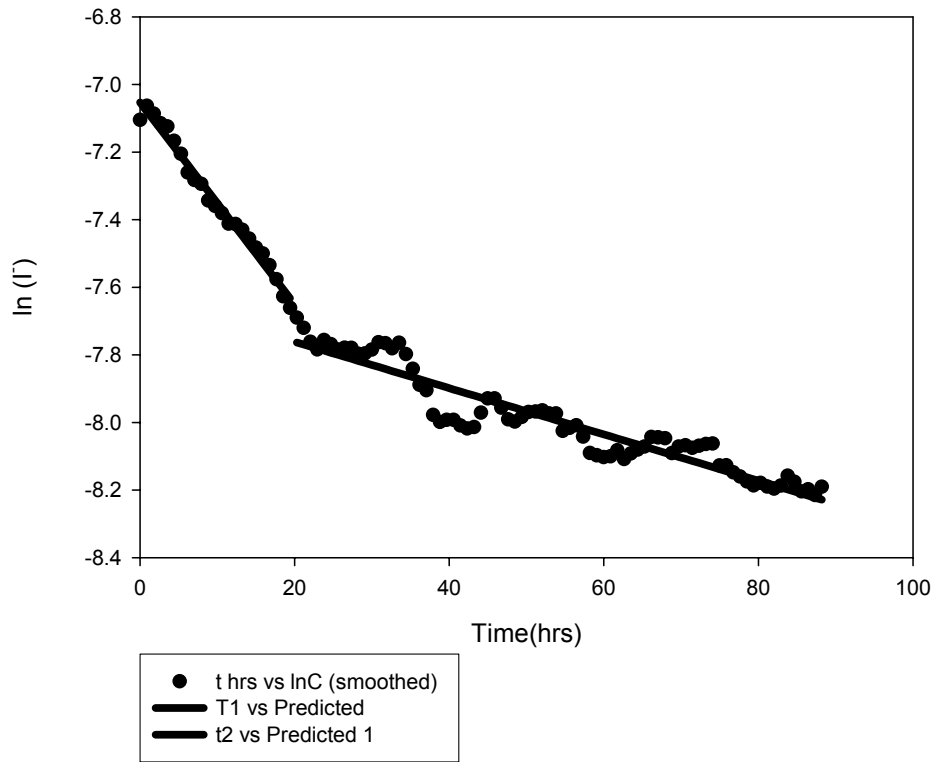
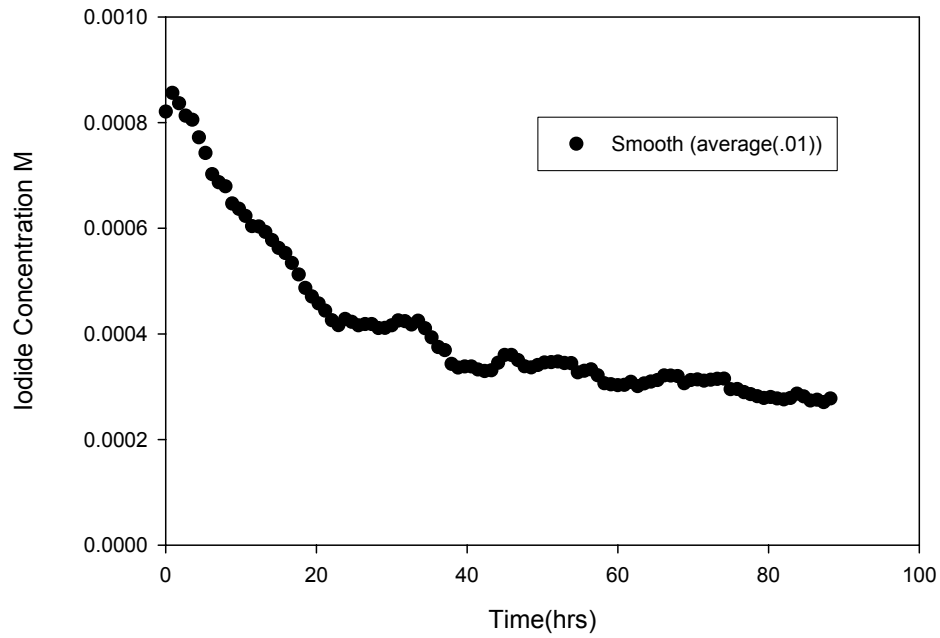
**Figure 2: Formation of  $I_2$  in 0.01M KI (pH 8.5) in the presence of  $MnO_2$  (Birnessite) at room temperature.**

Previously, it was demonstrated that phenolic compounds undergo aromatic substitution in the presence of iodine. With the availability of iodine acceptor such as p-hydroxybenzoic acid the loss of iodine can be followed with an iodide specific electrode. The results of one such study is shown below (Figure 3a). A 0.001 M solution of KI buffered with tris (50 mL) was allowed to react with 0.100 grams of  $\gamma$ - $MnO_2$  and 0.02M PHBA. The reaction resulted in transfer of iodide to the PHBA ring (aromatic substitution). The reaction sequence is as follows:



A plot of the natural logarithm of iodide concentration (Figure 3b) indicates that the reaction appears to slow with time. Since the PHBA and  $MnO_2$  are both in excess, the slowing in reaction may reflect a deactivation of the surface of the manganese (II) oxide.

Tris pH 7 PHBA (0.14g/50 mL)  
 $\gamma\text{MnO}_2$ (0.1g/50 mL)



**Figure 3a:** Iodide concentration is plotted as a function of reaction time for an 0.001 M KI solution buffered with tris. PHBA is 0.02 M and with 0.1 g of  $\text{MnO}_2$ . **Figure 3b:** The data is plotted as the natural logarithm of iodide concentration with time. Two “first order” regions are apparent.