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Immobilization of Fission Iodine by Reaction with a Fullerene Containing Carbon Compound and Insoluble Natural Organic Matrix: Quaterly Report October-December 2004

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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

We have conducted a large number of experiments to determine the possible reaction of iodate with sphagnum peat moss. These experiments indicate that the natural organic material reacts with iodate resulting in the formation of organically bound iodine and/or iodide in solution.

In the last quarter, we have conducted a number of experiments at various pHs and several temperatures (70oC, 60°C and 40°C). The reaction of iodate with peat follows pseudo first-order kinetics, although the reaction rate does appear to decrease significantly with reaction time. As noted in a previous report organically bound iodine appears to go through a maximum with reaction time indicating that it is eventually released into the solution as iodide. The stability of the organo-iodine intermediate appears to be a function of pH and temperature, as is the reaction rate of iodate with peat.

We tested the notion that iodate was first reduced to hypoiodic acid, which either reacts with phenolic moieties in the peat matrix or is further reduced to iodide. Heating experiments were conducted in the presence of N, N-dimethylamino benzene (NNDMA). This reagent reacts rapidly with hypoiodic acid and iodine forming of p-iodo- N, N-dimethylamino benzene (I-NNDMA). This product can be extracted and identified by GC/MS. I-NNDMA was detected in several experiments confirming the formation of HOI or I_2. Results from an experiment where 350 mg of peat was exposed to 20 mL of a 100 ppm iodate solution are shown in Figure 1. The experiment was conducted at pH 5.3 and 60°C. As shown in the figure, the amount of I-NNDMA was significantly lower that the quantity of iodate lost. The calculated I-NNDMA (from iodate loss) that is shown in Figure 1 assumes that all of the iodate lost was converted to IOH that was subsequently trapped by reaction with NNDMA. The actual measurements are considerable lower. This result indicates that IOH is not the exclusive intermediate, or that the peat is competing with NNDMA
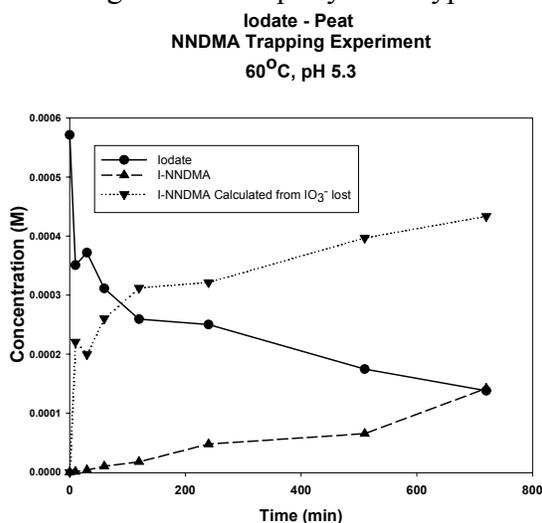

**Iodate - Peat
NNDMA Trapping Experiment
60°C, pH 5.3**

Legend:
- Iodate
- I-NNDMA
- I-NNDMA Calculated from IO_3^- lost

Figure 1: IOH trapping experiment. Reaction of iodate and peat at 60° C.

for IOH. We believe that there is a set of highly reactive functional groups that are "used up" early in the experiments. After these reactive groups are depleted the NNDMA becomes the main sink for IOH. Note that the slope of the I-NNDMA line and the slope of the I-NNMA calculated line are about the same after 120 hours.

We also examined the possible influence of oxygen on product distributions from the iodate experiments. Reactions were carried out in a continuous stirred water-jacketed batch reactor. The iodate, peat and buffer concentrations were the same as previous experiments (that were carried out in glass screw cap test tubes) that were heated in an oven. There were no special measures taken to eliminate oxygen in the test tube experiments. The batch reactor experiments were heated using a circulating water bath. The batch reactor was continuously sparged with nitrogen during the reaction. The sparge gas was passed through an impinger filled with either dilute NaOH or $NaHSO_3$ to determine if any iodine (I_2) was lost from the system. Initial reaction rates did seem faster in the stirred reactor, however we believe this resulted from constant stirring in the batch reactor rather than the absence of oxygen. The overall extent of iodate reduction was about the same in both systems. Our results indicate that I_2 was not sparged from the system under these conditions (pH 2-9 at 60^oC) so that IOH is most likely the iodinating species produced by the reduction of iodate.

Our data that indicates that iodate is first converted to hypoiodic acid (or iodine), which in turn, can be further reduced to iodide, or react with peat resulting in sequestration into the organic matrix. This reaction presumably occurs as a substitution for hydrogen at phenolic rings. The reaction of iodate with peat appears to involve competition (parallel reactions) between sequestration and reduction to iodide.

Our previous results demonstrated that methyl iodide was produced by pyrolysis of iodine or iodate treated peat. We proposed that iodine could be recovered and purified chromatographically and that the purified methyl iodide could be converted to NaI for transmutation or storage. The packed column gas chromatograph that will be used for these studies was received during this last reporting period. The instrument is an SRI 8010 with a TCD detector and injector valve equipped with a thermal desorber. The thermal desorber has a trap packed with carbosieve. Volatile materials that are collected on the carbosieve trap can be t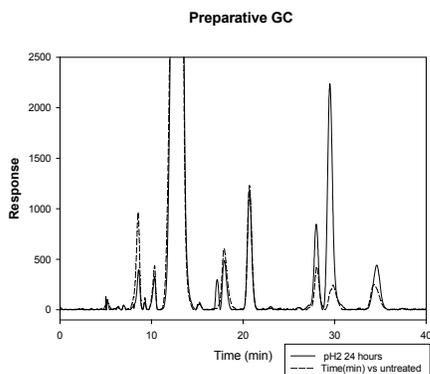ransferred to the gas chromatograph by actuating the valve and activating the thermal desorption oven. In order to scale up our pyrolysis experiments we obtained a 6" tube furnace manufactured by Carbolyte. This programmable furnace has a 0.5" diameter process tube that can hold 8-100 mg samples of peat or ion exchange resin. The furnace is connected to a source of helium with Swagelok™ fittings. During sample heating a helium stream sweeps products from the tube furnace to the carbosieve trap located in the thermal desorber unit. Chromatography is initiated by thermally desorbing trapped volatiles from the carbosieve trap to the GC

Figure 2: Comparison of a chromatogram from a peat exposed to iodate for 24 hours with an unreacted sample.

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column (2mm x 2m, Porapak Q). The instrument was calibrated with by injecting methyl iodide into the thermal desorber trap. The response factor and retention time of methyl iodide were thus determined. Pyrolysis experiments with 8-12 mg of peat of been conducted using this experimental apparatus. In Figure 2 we compare the results for 10 mg of iodate treated peat (pH 2, 24 hours) with the results from untreated peat. We have examined recovery from both iodine and iodate treated peat samples. Our results indicate that 40-70% of the bound iodide can be recovered by this procedure.

In a previous report we demonstrated that ballistic heating of iodinated resin to 500°C released methyl iodide (reaction 1). The competitive reaction results in the release of trimethylamine (reaction 2).

**Reaction 1: Formation of methyl iodide using AG-1 resin.**
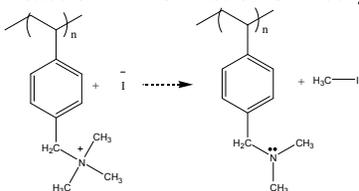
**Reaction 2: Formation of trimethylamine from AG-1 resin.**
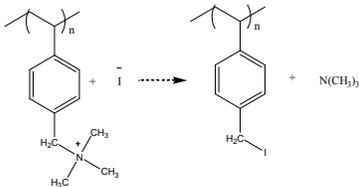
During this last quarter we obtained results with resins exposed to different concentrations of iodide. The results indicate that methyl iodide yield at 500°C is a linear function of iodide concentration. We believe this could serve as the basis for an analytical measurement of iodine. We have also examined thermal decomposition of the AG-1 anion exchange resin using the preparative gas chromatography and tube furnace. At 300 to 600°C only trimethylamine was observed. This is because of the slow heating rate of the tube furnace and the more rapid loss of trimethylamine at lower temperatures. We are therefore continuing to examine other resins for this application.

Previous reports disclosed that pyrolysis of peat moss that was used for trapping iodine produced a substantial amount of volatile and reactive methyl iodide (MeI). In addition, the reaction of peat with iodine also produces iodide that will need to be trapped and converted to NaI. The methyl iodide produced during pyrolysis can be purified chromatographically. It will need to be converted to NaI for subsequent transmutation. We will be exploring the Wurtz reaction for this purpose. We are exploring the use of resins for two purposes: 1. Trapping of iodide from aqueous solution with subsequent pyrolysis of the resin to produce methyl iodide. 2. Capturing methyl iodide from the gas phase so that it can be converted to NaI.

We are exploring two approaches. (1) The use of poly-(4-vinylpyridine-co-divinylbenzene), **1**, (PVP) to react with MeI or, in its quaternary ammonium ion form, **2** or **3**, and to exchange with a counter ion, **A⁻**, to trap iodide ion after hydrolysis of MeI. (Scheme 1.) A key point here is the equilibrium point of the reaction **2 ↔ 3**. (2) A second approach is to employ a polymeric sulfide, **4**, to trap MeI as a sulfonium salt, **5**, which could then be treated with sodium hydroxide to liberate volatile methanol and form non-volatile sodium iodide and regenerate **4**. The polymeric sulfide, **4**, could then be recycled (Scheme 2).
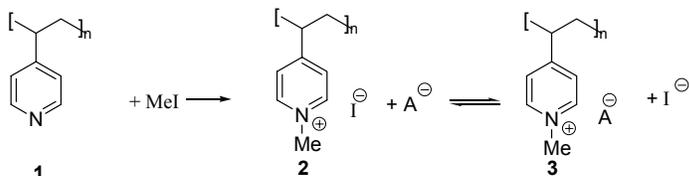
Scheme 1 Trapping MeI using PVP
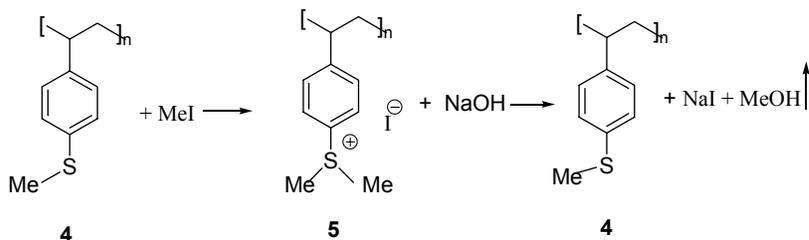
Scheme 2 Capturing MeI and breaking it down to non-volatile NaI and volatile methanol

At this point commercially available PVP, **1**, has been obtained and quaternary ammonium ions, **2** and **3**, with counter ions p-toluensulfonate and methyl sulfate have been prepared. The sulfide resin, **4**, has been synthesized.