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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 2005

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Quarterly Report for January, February and March 2005

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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 continued experiments on the reaction of iodate with sphagnum peat moss. We have established that iodate added to a suspension of peat moss undergoes reduction and to a significant extent is incorporated into the peat moss. We have confirmed the incorporation of iodine into the peat matrix using pyrolysis GC/MS. In addition, we have performed a scaled up pyrolysis using the preparative GC system that was described in a previous report. This instrument consisted of a packed column gas chromatograph (SRI 8010) with a TCD detector and injector valve equipped with a thermal desorber. Pyrolysis experiments were performed in 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. During sample heating helium stream sweeps products from the tube furnace to the carbosieve trap located in the thermal desorber unit. Volatile materials that are collected on the carbosieve trap can be transferred to the gas chromatograph by actuating the valve and activating the thermal desorption oven. Chromatography is initiated by thermally desorbing trapped volatiles from the carbosieve trap to the GC 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 organic matter have been conducted using this experimental apparatus. Experimental results for a two series of incubations are shown in Figure 1. Results for experiments with a peat sample incubated at 40°C and pH 4.3 are shown. In addition, the results for a commercially available humic acid at pH 2 are presented. The low pH was used to prevent dissolution of the humic material.

During this last quarter we have investigated the influence of pyrolysis temperature on the yield of methyl iodide. We have done experiments with the analytical pyrolysis unit described in previous reports and with the preparative GC. The results of these studies are illustrated in Figures 2 and 3 and demonstrate optimum methyl iodide production at 400°C. The peat (350 mg) was incubated in 20 mL of $2.7 \times 10^{-3} \text{M KIO}_3$. The suspension pH was established with phosphate buffer and the sample was held in a constant temperature incubator. In most cases the amount of methyl iodide produced by pyrolysis increased with an increase in heating time. Previous reports indicated that organically bound iodine went through a maximum during heating experiments and then slowly decreased. This maximum was not apparent in the pyrolysis results.

We have conducted additional kinetic experiments on the reaction of natural organic matter with iodine. These experiments were conducted in aqueous solution and the progress of the reaction was monitored by UV spectroscopy. In previous experiments we added iodine to aqueous buffers. Because of rapid reaction kinetics the rates of reaction were often difficult to follow. In this latest group of experiments we have included a constant background of KI. The equilibrium constant for the formation of the I_3^- (aq) species is well known.



The presence of I^- (aq) converts I_2 (aq) to I_3^- (aq). Which has strong UV adsorption at 290 nm and 350 nm. Thus, the reaction of the aqueous iodine with various natural organic materials, or model compounds, can be followed by monitoring the decrease in absorbance at 290 or 350 nm. The reactive species in these experiments is still I_2 , however, because most of the iodine is tied up as the triiodide (I_3^-) species reaction rates are reduced by a factor of $(1+K[I^-])^{-1}$. Which makes following the reaction easier. Reactions of humic acid, soluble alkali lignin, vanillin and vanillic acid were studied. Example results for Aldrich alkali lignin are shown in Figure 4. These measurements were conducted in aqueous buffered solutions at room temperature ($\sim 20^\circ\text{C}$). The results in Figure 4 confirm previous observations an increase in reaction rate of lignin with iodine with increasing pH.

Previously we have hypothesized that iodine reacts with phenolic groups of lignin. Thus, NOM should exhibit a finite capacity for reactions. This is illustrated in Figure 5 where the reaction kinetics were monitored for three additions of iodine 3.1×10^{-5} M to the same solution of alkali lignin. With each addition the rate of loss of absorbance at 350 nm is reduced (note flattening of curve). The lignin concentration was (0.008 g/mL) for these experiments.

We have conducted additional measurements of the reaction of vanillin and vanillic acid (model compounds) under these reaction conditions. The reaction of these model compounds is apparently first order in iodine and in the phenolic model compounds (modeling results not shown). The reaction is faster at higher pH for vanillin and faster for the vanillic acid than the vanillin. In the case of vanillin, the UV spectra indicated that Iodo-vanillin was the major product. The substantial adsorption of both the product and the starting material at 290 and 350 made measurements of vanillin kinetics difficult. We found that the background adsorption at 350 and 290 nm (the adsorption maximum for triiodide) shifted substantially as a result of the formation of iodovanillin and made interpretation of measurements difficult. We monitored the reaction of I_3^- with vanillin at isosbestic points (for vanillin and iodo-vanillin) where substantial I_3^- absorption was still apparent. The isosbestic points have to be determined at each pH studied, as the UV spectra for ionizable compounds are pH dependent. For pH 8.1, measurements could be made at 282 nm (close to the 290 maximum for triiodide). At pH 6.9 measurements were made at 269 nm (considerable off the maximum for triiodide). This explains the difference in starting absorbance for the pH 8.1 and pH 6.9 results of figure 6. Previously we thought that the ionization of the phenolic proton was important for promoting the

reaction. The pKa of the vanillin hydroxyl group is 7.4. Thus at pH 8.1 the phenolate is the dominant species. At pH 6.9 the concentration of the phenolate is reduced and this is reflected in the slower reaction kinetics. The pKa of the vanillic acid phenolic hydroxyl group is closer to 10. Therefore the phenolate is a minor species at pH 8.1. The oxidation of the electron withdrawing aldehyde (carbonyl) group of vanillin to the carboxylic acid (vanillic acid) seems to more than compensate low ionization of the phenolic hydroxyl in vanillic acid, as the reaction of vanillic acid with I_3^- is considerable faster than with vanillin. We will investigate additional pH values for this compound.

Methyl Iodide Production from Natural Organic Matter after reaction with IO_3^-

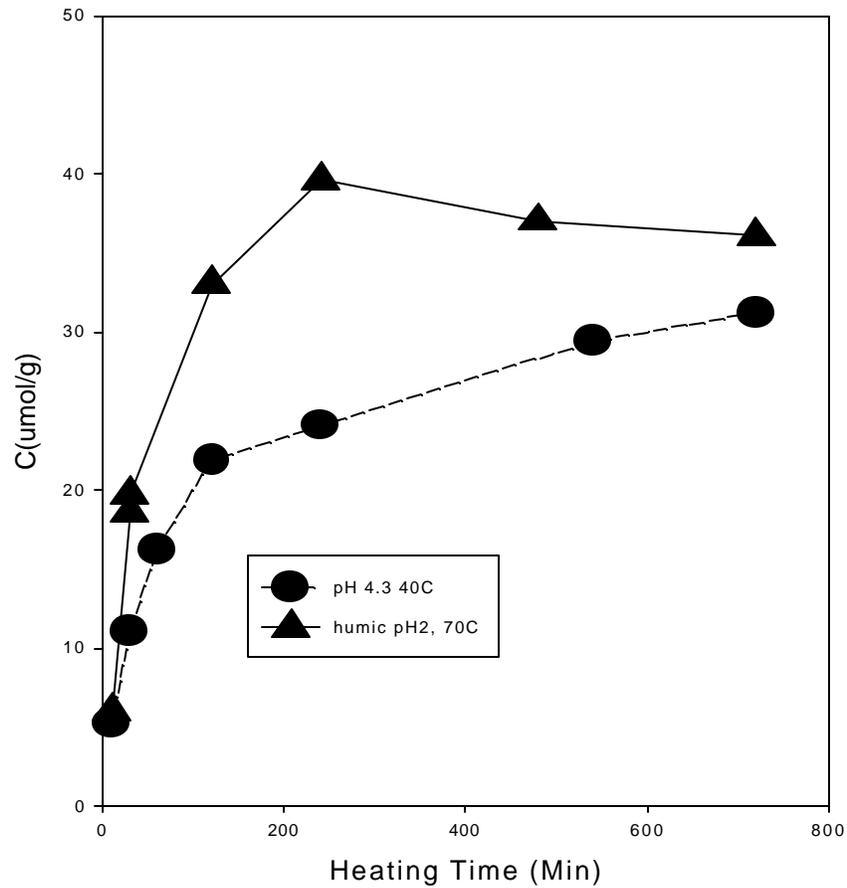


Figure 1: Methyl Iodide production from pyrolysis of sphagnum peat and a commercial (Flucka) humic acid exposed to a KIO_3 solution for various times.

Analytical Pyrolysis of Iodate Treated Peat

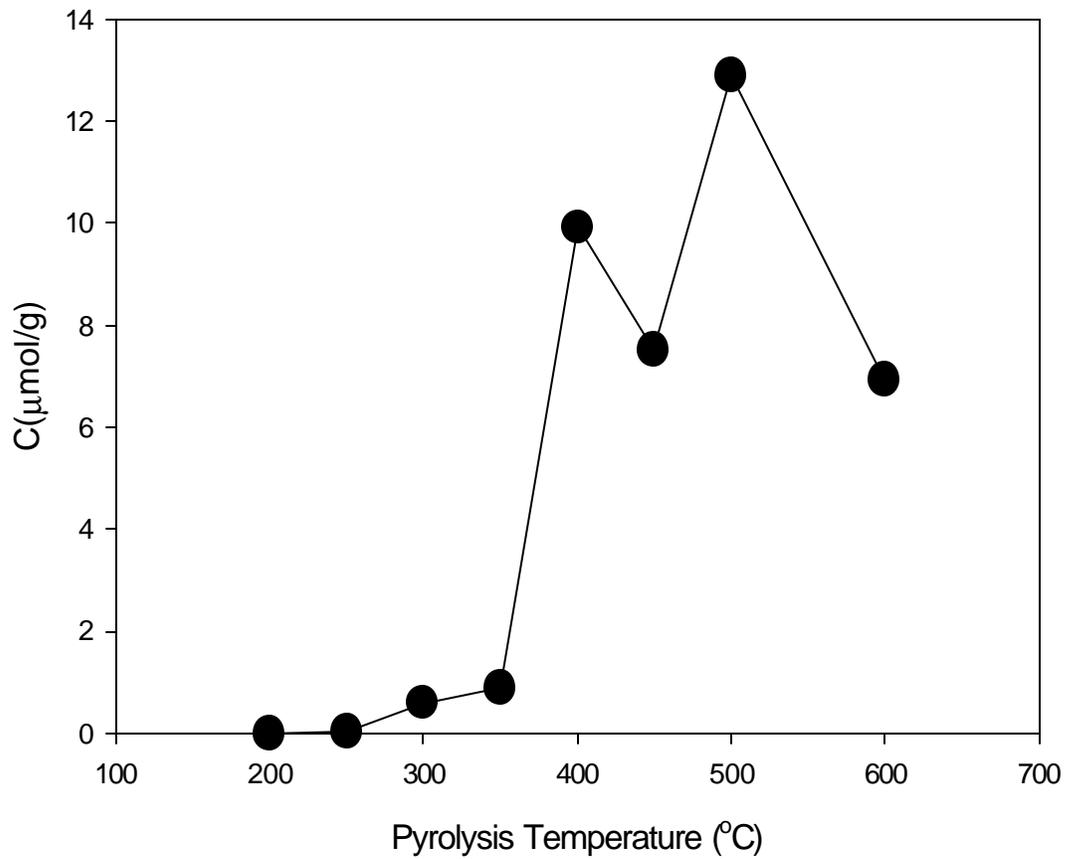


Figure 2: Methyl Iodide produced during analytical pyrolysis of a KIO_3 treated peat sample. The results indicate maximum methyl iodide production at 400-500 $^{\circ}\text{C}$.

Methyl Iodide Pyrolysis Yield Iodate Treated

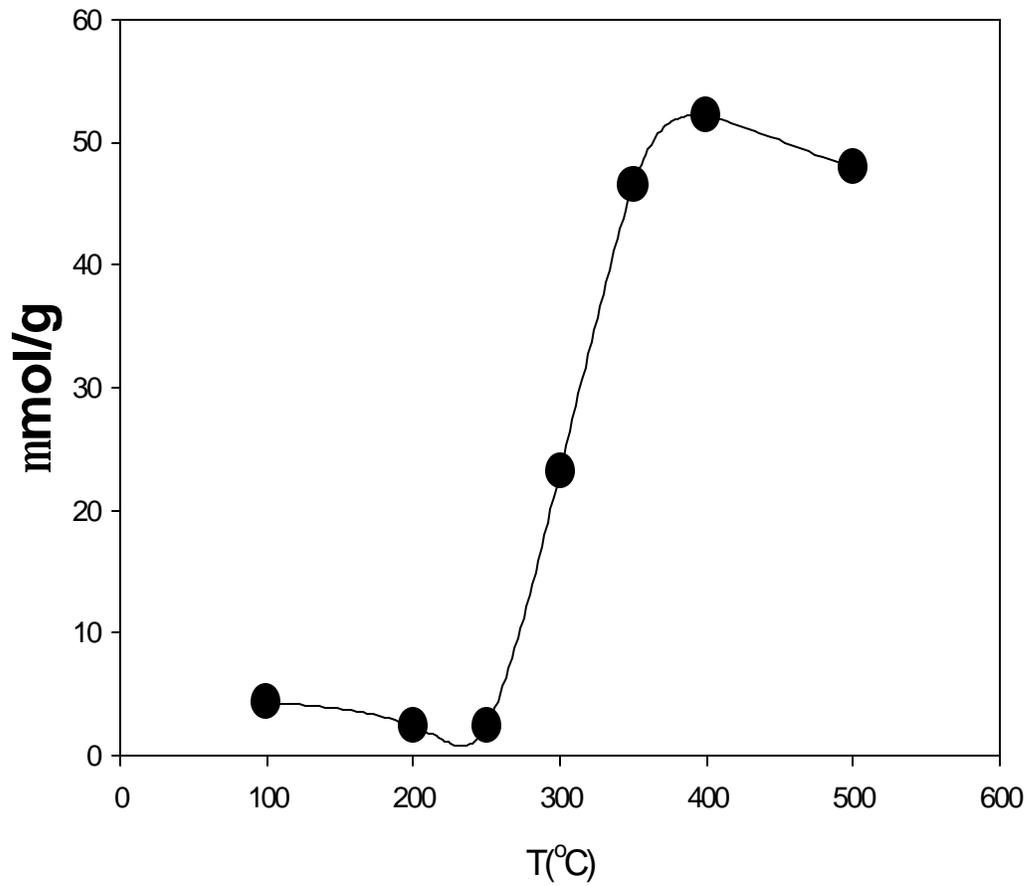


Figure 3: Methyl Iodide production during “preparative” pyrolysis of a peat sample treated with KIO_3 . Maximum recovery at 400°C is indicated.

Reaction of I_2 (as I_3^-) with Alkali Lignin (0.08 mg/mL) in
0.10 M KI

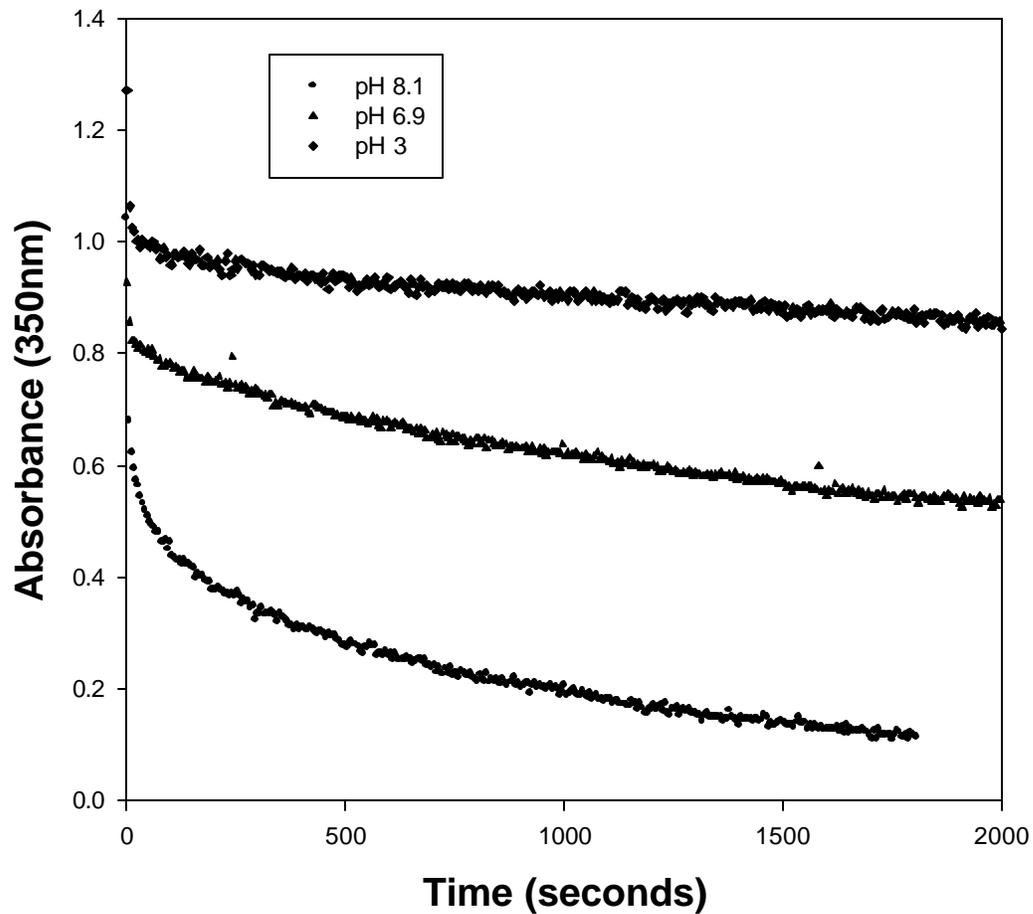


Figure 4: The reaction of I_3^- with commercially available alkali lignin is monitored at three different pH values. The reaction rate increases with increasing pH.

Repeat Application of Iodine at pH 8.2

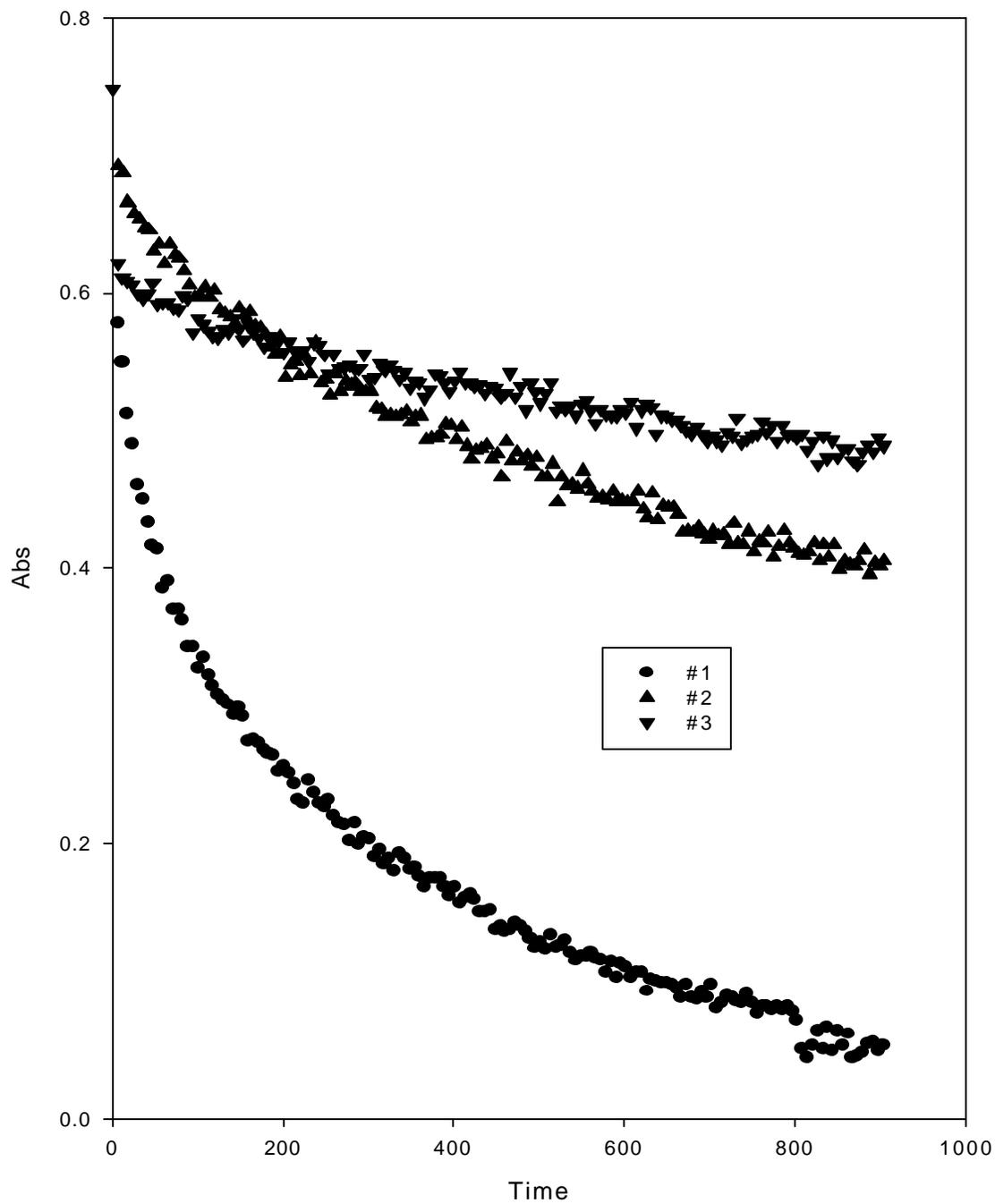


Figure 5: The finite capacity of lignin for iodine is indicated by repeated treatment of the same sample with iodine. The reaction rate decreased with each treatment. By the third treatment only small fraction of the iodine added was removed.

Reaction of Vanillin and Vanillic Acid with I_3^-

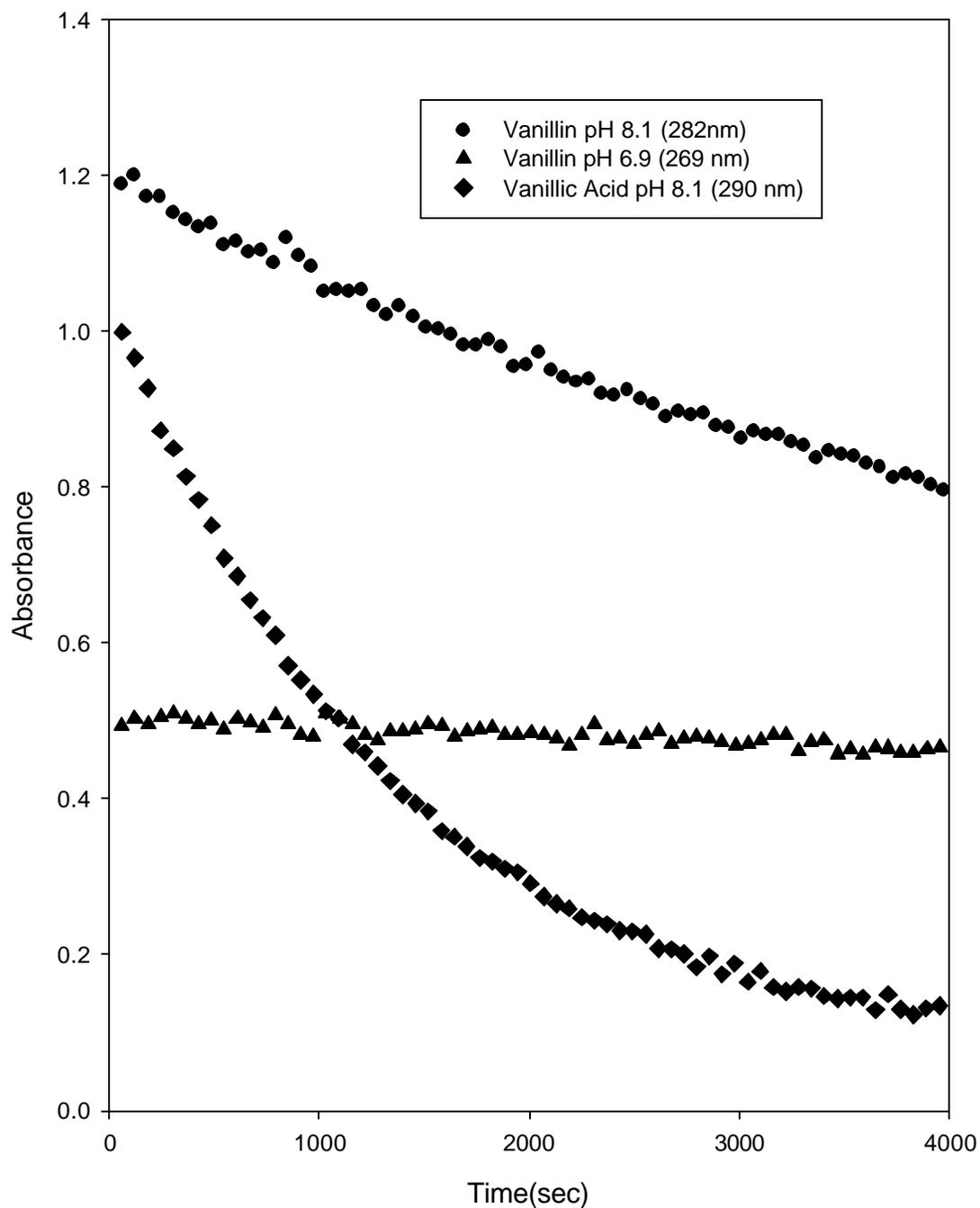


Figure 6: The reaction of iodine (as I_3^-) was examined for two lignin model compounds. Different wavelengths were used because of differences in the background absorption of the model compounds. The initial slopes indicate the reaction rates, of these compounds.