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Identification of volatile iron species generated by UV photolysis

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ABSTRACT

The volatile products of photochemical generation (PVG) of iron from solutions of formic or acetic acids were examined by GC-MS. Iron pentacarbonyl was the sole analytical species detected in both cases, as confirmed by comparison of the results with a NIST reference spectrum. Silylation of the interior surfaces of the quartz PVG tubing essentially eliminated memory effects within the reactor such that signal duration was determined simply by the residence time of the sample solution.

1. INTRODUCTION

The use of chemical vapor generation (CVG) as a sample introduction methodology for atomic spectrometry is a well established procedure used for the determination of a number of elements at trace and ultratrace levels. Several techniques can be used to generate volatile species, as recently reviewed by Sturgeon *et al.* and Wu *et al.* [1, 2] and include cold vapor, halide, oxide, hydride, carbonyl, alkyl and chelate generation.

Most recently, UV photochemical vapor generation (PVG) has arisen [3, 4] as a promising alternative to CVG as it is easily implemented, is inexpensive and has potential for enhanced LODs, reduced H₂ production and greener analytical chemistry. This technique is based on the generation of reactive free radicals by the application of ultraviolet light to solutions of the element of interest containing a low molecular weight organic acid.

To date, analytical applications of PVG have been undertaken for only a few analytes, in both continuous flow and batch systems, including Fe in biological samples and water [5, 6], iodine in milk powder, biological samples and soil [7], and Hg in biological samples [8, 9], as well as water [10] and wine or liquor [11]. Clearly, more effort needs to be expended in pursuing applications but the interest at this time lies predominantly in further expansion of the suite of elements amenable to PVG.

Little is known of the mechanisms of PVG apart from the identity of the volatile reaction products, which include cold vapor Hg [8 – 11], analyte hydrides [12 - 14], as well as alkylated [14, 15] and carbonylated [16, 17] species detected by impact (EI) and electrospray ionization (ESI) mass spectrometry with GC or LC sample introduction. In order for significant progress to be made in this emerging area, it is necessary that more fundamental information be acquired and identification of the reaction products is the first step in this direction. The aim of this study was to elucidate the identity of products formed during the photochemical vapor generation of iron.

2. EXPERIMENTAL SECTION

2.1 Instrumentation

Photoreduction was accomplished using a 17.4 W low pressure UV mercury grid lamp (Analamp, Claremont, CA) onto which quartz tubing (25 cm x 25 cm mm i.d x 2.5 mm o.d: 4 ml internal volume) was overlain and countered in such way as to match the geometry of the UV discharge lamp. The UV grid lamp was 'warmed' for 30 minutes prior to starting any experiments.

A schematic of this system is presented in Figure 1.

For species identification purposes, vapor generation was performed in an off-line mode in a fume hood. Samples were passed through the quartz tubing with the aid of a four channel miniplus 2 peristaltic pump (Gilson, Middleton, WI), providing a continuous mode of vapor generation. The residence time of the analyte solution exposed to UV was about 250 s. Ar was used as a carrier gas at a flow of approximately 100 ml/min. The gaseous reaction products were phase separated in a gas-liquid separator and subsequently transported through a 250 ml glass gas sampling cylinder fitted with stopcocks at each end and a septum port for gas sampling. After 10 minutes of continuous purging with the effluent from the gas/liquid separator, the stopcocks were closed and the gas phase containing the iron species subsequently sampled with a gastight syringe and injected into the GC-MS for species identification.

A Varian model CP-3800 gas chromatograph, interfaced to a Saturn 2200 mass selective detector (mass range 50-350 Da), was employed to identify the reaction products. Iron compounds were separated on a 30 m x 0.25 mm id x 0.25 mm film (J&W Scientific) DB5 capillary column (5% phenyl, 95% methylpolysiloxane) using UHP helium carrier gas and an electronic head pressure control. Split sample injection (1:50) was used with a

0.4 ml injection volume. The injector and transfer line temperatures were 120 and 240°C, respectively. The carrier gas flow rate was set at 1.0 ml min⁻¹. An 13 min temperature program was used with an initial temperature of 40°C and a hold time of 4 min, followed by a ramp of 25°C min⁻¹ to a temperature of 245°C, which was held for 0.8 min.

Prior to the GC-MS experiments, the glass sampler was flushed with Ar for about 5 min at room temperature in order to remove any air entrained in the system and eliminate memory effects. A blank response was measured before each analytical run using solutions containing only the low molecular weight organic acids. Compounds were identified by comparison of their GC mass spectra with those obtained from the NIST database.

2.2 Reagents and Solutions

Formic and acetic acids were obtained from Anachemia (Canada) and used without purification. High purity deionized water (DIW) was produced by reverse osmosis of tap water followed by deionization (Barnstead/ Thermolyne, Dubuque, IA, USA) to yield 18 MΩ cm resistivity reagent. All other chemicals used were of analytical reagent grade. Working solutions were prepared daily by diluting 1000 mg l⁻¹ stock solutions of Fe in the appropriate low molecular weight acids.

2.3 Safety considerations

The full range of Fe compounds produced in this study may not be known. Essential safety precautions must be taken during all manipulations and an adequate ventilation/exhaust system must be used. All manipulations of gaseous Fe species were performed in a fume hood.

3. RESULTS AND DISCUSSION

3.1 Identification of volatile iron species generated by UV photolysis

As reported earlier [6], an irradiation time of about 250 s is needed to photochemically generate volatile iron compounds in the presence of low molecular weight organic acids. Such a long irradiation time can result in the formation of numerous bubbles in the photoreactor likely due to the formation of gaseous photolysis products such hydrogen, carbon monoxide and dioxide and methane as well as the volatile analyte species. A generation efficiency of about 60% could be reached as earlier verified by ICP-OES studies [6] wherein temperature, pH and formic acid concentration were concluded to be the most important factors for photochemical vapor generation of iron and the mechanism may involve an initial reduction of ionic iron to free atoms in solution with concurrent generation of and attack by organic radicals.

When exposing a 200 ppm solution of Fe containing 50 % formic acid adjusted to pH 3 to the UV source, a single sharp peak having a GC retention time of about 2.5 min was obtained. No such peak arises when processing of a blank, suggesting the presence of a volatile iron containing species.

Figure 2 shows the corresponding EI mass spectrum. Fragments containing iron are easily identified in the mass spectra as a result of their characteristic isotopic pattern (Fe^{54} (5.8%), Fe^{56} (91.72%), Fe^{57} (2.2%), Fe^{58} (0.28%)). Other major fragments were observed at m/z 84, 112, 140, 168 and 196. These peaks have mass fragment ions spaced 28 Da apart, suggesting the addition a CO ligand to each fragment, thereby implying the presence of iron pentacarbonyl at m/z 196. This was confirmed by comparing the experimental mass spectrum with one from the NIST EI mass spectral database. It may be concluded that the volatile iron -containing species produced by UV photogeneration of iron in the presence of formic acid is $\text{Fe}(\text{CO})_5$. Iron pentacarbonyl, $\text{Fe}(\text{CO})_5$, is a known compound and a common precursor to diverse iron compounds. It's an insoluble, volatile and stable species readily formed by the action of carbon monoxide on reduced

iron. Additional peaks in the experimental mass spectra appeared at m/z 74 and 102, not present in the NIST database spectrum, may correspond to water adducts such as $\text{Fe}(\text{H}_2\text{O})$ and $\text{FeCO}(\text{H}_2\text{O})$ as a consequence of the aqueous medium from which this material was synthesized..

In an earlier study [6] it was noted that vapor generation efficiency in the presence of acetic acid was poor, possibly owing to the manner in which discrete sample volumes were introduced to the photoreactor and subjected to a predetermined irradiation time before sweeping the contents to the phase separator. In this study, a continuous mode of generation of volatile iron compounds was used and the formation of volatile iron in the presence of 50% acetic acid adjusted to pH 3 was examined. In this case, a single sharp peak with a retention time of about 2.5 min was evident in the GC-MS chromatogram having an EI mass spectrum similar to that observed for the formic acid system. Figure 3 reveals fragments corresponding to Fe^+ at m/z 54, 56, 57 and 58 with additional major fragments at m/z 84, 112, 140, 168 and 196 corresponding to FeCO , $\text{Fe}(\text{CO})_2$, $\text{Fe}(\text{CO})_3$, $\text{Fe}(\text{CO})_4$ and $\text{Fe}(\text{CO})_5$, respectively. These results support the conclusion that in the presence of acetic acid, formation of $\text{Fe}(\text{CO})_5$ occurs. The relative intensities are 2.5-fold lower than those obtained when generation occurs from a formic acid medium.

The $\text{Fe}(\text{CO})_5$ was found to be stable over a period of 20 h at room temperature as no detectable losses occurred during that period. Similar behavior was earlier reported for Ni [16].

3.2 Memory Effect

The PVG of Fe suffers from an extensive memory effect with the need for long washout times (about 60 min) of the quartz reaction tubing before background levels can be reached, which makes the use of this technique as an analytical tool somewhat impractical. Different washing solutions, including ammonium hydroxide, formic acid,

acetic acid and tetramethylammonium (TMAH) were examined, but no significant reduction in the washout time was achieved.

The inner surface of the quartz tube was silylated in order to deactivate internal surfaces [18]. This was achieved by flushing the quartz tubing with a 10% solution of dimethyldichlorosilane (Pierce Chemical Co) in toluene followed by successive rinses with toluene and methanol. This procedure was repeated three times and the surfaces were then dried at room temperature in a stream of N₂. With this treatment, the memory effect was substantially reduced; background levels could be reached after 5 minutes, corresponding to the time required to simply propel the sample through the tubing at a rate of 1 ml/min. It was verified that the deactivation of the internal surfaces with the silylate reagent was effective over a period of several days of intense work, and once the washout time reach twice the initial time (i.e, 10 min), the inner surface of the quartz tube was again deactivated. No change of sensitivity was observed after the silylation of the inner surface of the quartz cell.

4. CONCLUSIONS

This study provides identification of volatile iron species by UV photo-reduction in the presence of low molecular weight organic acids. The volatile product is identified by EI mass spectrometry as iron pentacarbonyl. Memory effects relevant to the photo-CVG of iron were eliminated with silylation of the inner surface of the quartz tube.

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Figure Captions

Figure 1. Schematic diagram of the experimental setup

Figure 2. EI mass spectrum of the compound eluting at 2.5 min for 200 ppm Fe in 50% formic acid pH 3

Figure 3. EI mass spectrum of the compound eluting at 2.5 min for 200 ppm Fe in 50% acetic acid pH 3

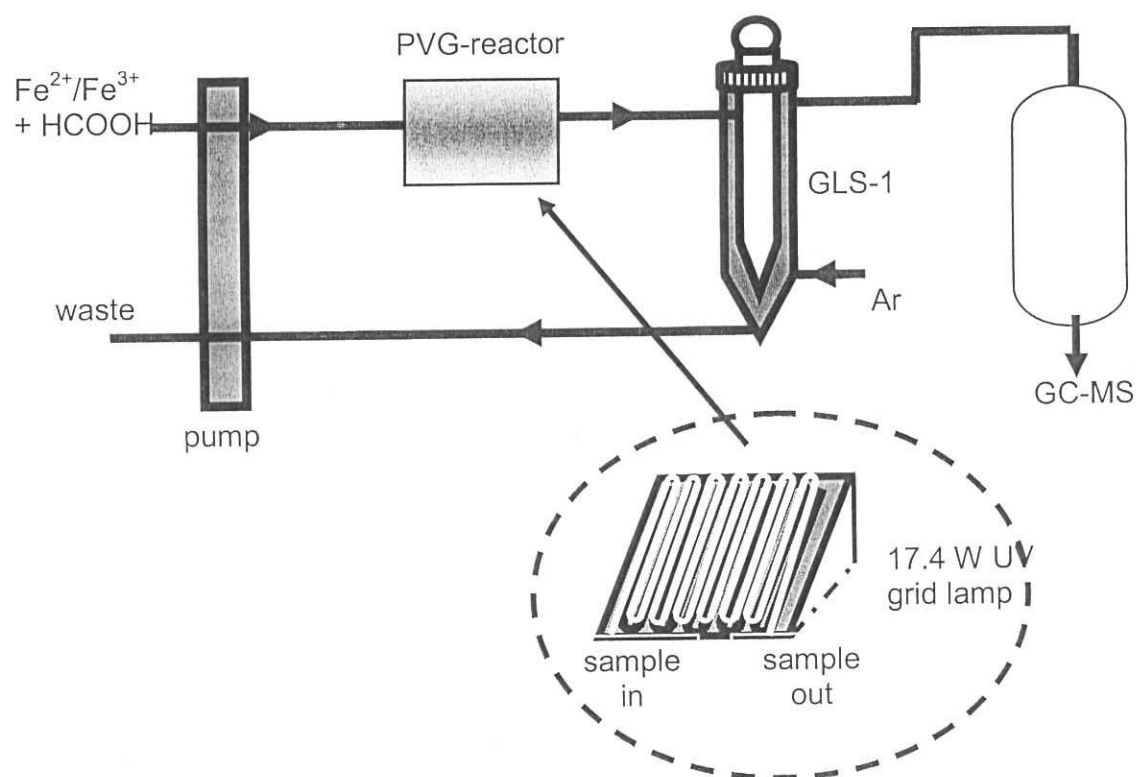


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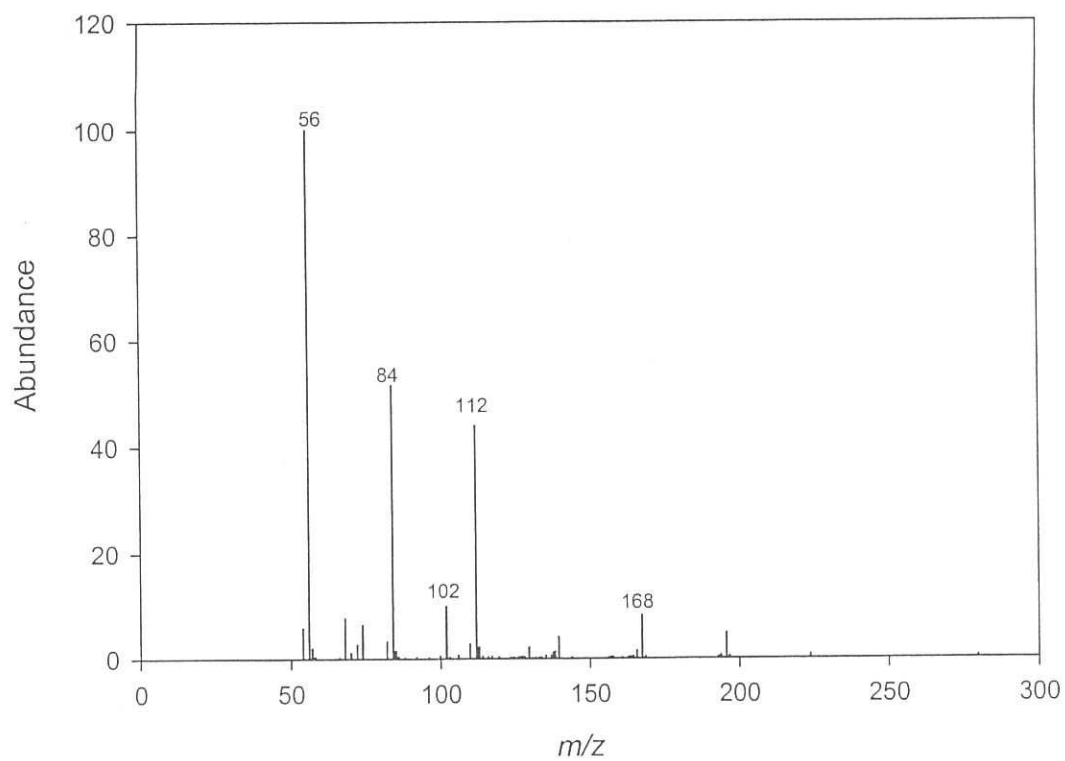


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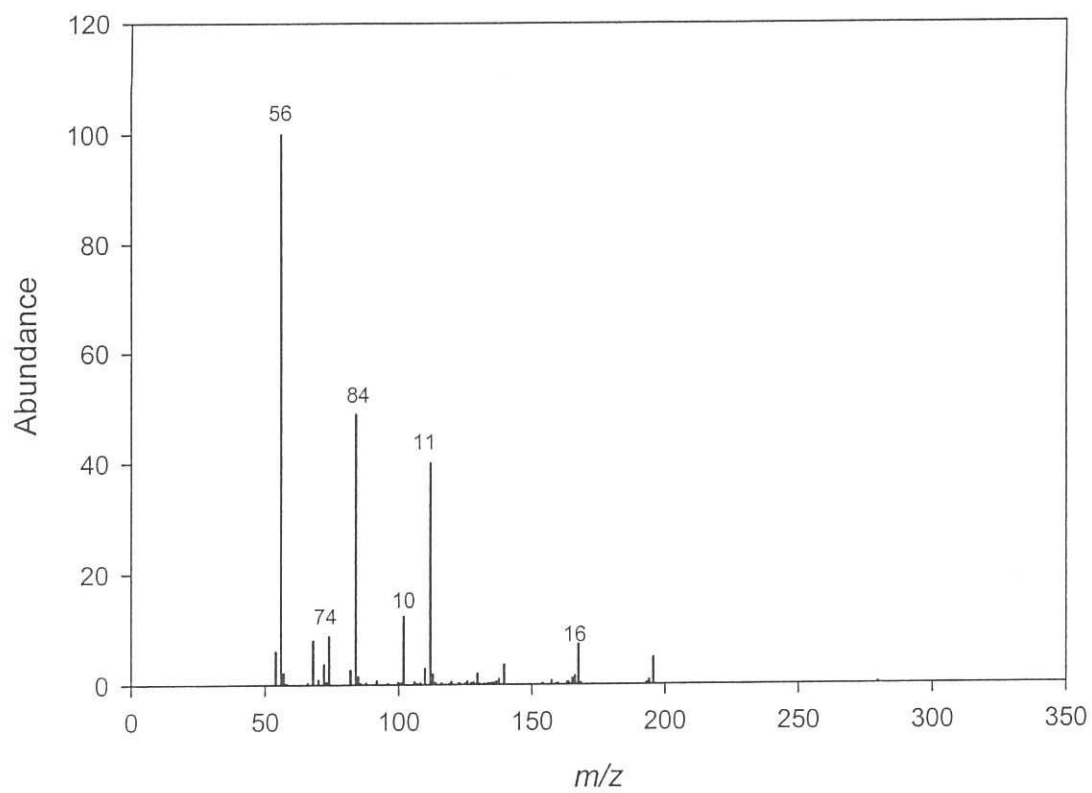


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