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UV light-mediated alkylation of inorganic selenium

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In the presence of low molecular weight organic acids (formic, acetic, propionic and malonic), inorganic selenium(IV) is converted by UV irradiation to volatile selenium carbonyl, dimethylselenide and diethylselenide, depending on the acid used. Gas chromatography–mass spectrometry analysis of the volatile products shows that, in 0.7 M formic acid solution, approximately 60–70% (*v*/*v*) SeH_2 and 30–40% (*v*/*v*) SeCO are formed. The presence of nitrate ion appears to increase threefold the formation of SeCO while completely suppressing formation of SeH_2. Copyright © 2003 Crown in the right of Canada. Published by John Wiley & Sons, Ltd.

KEYWORDS: selenium; alkylation; organic acids; UV irradiation

INTRODUCTION

There is wide interest in the syntheses of various low molecular weight dialkyl selenium compounds in the semiconductor industry for vapor deposition purposes.[1] Typical synthetic routes usually involve the reaction of selenide ions with appropriate alkylhalides in an aqueous environment, producing dialkylselenides in good yield. Dialkylselenides are often present as by-products during the preparation of selenols.[2] There are reports of reacting selenium hydride (SeH_2) with ethylene at 350 °C and 120 atm to produce diethylselenide.[3]

Bio-methylation of selenium in soils, sediments, plants, fresh water systems and the marine environment into dimethylselenide is considered to be a major source of atmospheric selenium.[4,5] Although emphasis has been placed on bio-methylation, parallel photochemical processes abound in nature. A methylchromium bond was shown to be formed during the photolysis of tertiary-butoxy radicals and chromium(II) in aqueous solution.[6] In the presence of acetate ion or acetic acid, aqueous solutions of Hg^{2+} give rise to methylmercury following photolysis in sunlight.[7] In the case of selenium, use of a TiO_2 photocatalyst and UV irradiation permitted removal of selenate ions from an aqueous solution, presumably by formation of volatile SeH_2.[8]

Results presented here demonstrate that photochemical alkylation by UV light serves as a new pathway for the transformation of inorganic selenium to its volatile carbonyl, methylated, or ethylated analogues.

EXPERIMENTAL

Instrumentation

A flow-through photoreactor, consisting of a 5 m length of 1.1 mm i.d. polytetrafluoroethylene (PTFE) tubing (Alpha Wire Corp., New Jersey, USA) wrapped around a low-pressure mercury vapor UV lamp (254 nm, 15 W, Cole Parmer, USA) was constructed. Samples were pumped through the tubing at a flow rate of 2 ml min^{-1} with the aid of a peristaltic pump. A 55 ml min^{-1} flow of helium purge gas was introduced into a gas–liquid separator and merged with the effluent from the UV photoreactor, transporting the volatile species either directly to a heated quartz tube atomizer (QTA), or through an intermediate cryogenically cooled U-shaped pyrex condensation tube (0.8 cm i.d. × 0.6 cm i.d. × 13 cm deep × 4 cm across). The QTA temperature was maintained at 900 °C. A hydrogen flow rate of 15 ml min^{-1} was introduced via a second line into the atomizer to aid in the atomization of selenium. A schematic of the experimental system is illustrated in Fig. 1.

The QTA was mounted in the burner (optical) compartment of a Perkin–Elmer Model 4100 atomic absorption spectrometer fitted with a Perkin–Elmer electrodeless discharge lamp (EDL System II). The EDL was operated at 350 mA and radiation was detected at the resonance wavelength of 196.0 nm using a bandpass of 0.2 nm (low slit). Simultaneous deuterium background correction was applied for all measurements.

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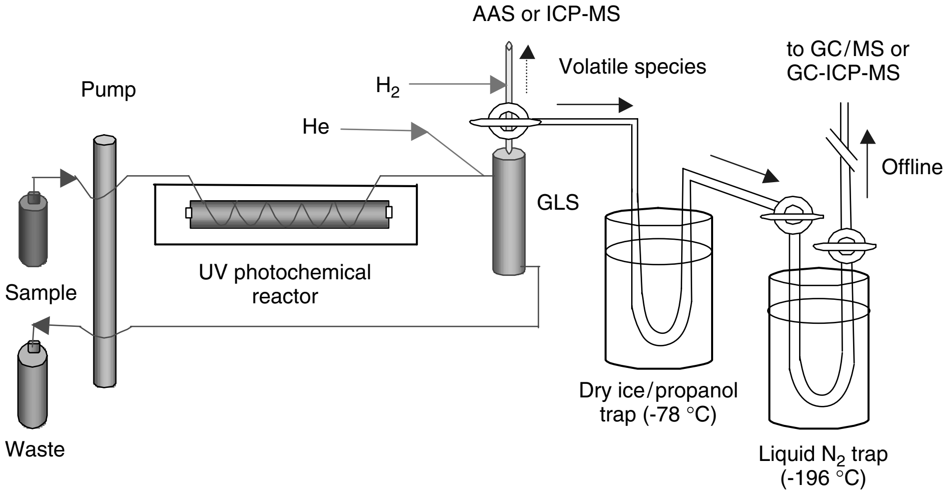

Figure 1. Schematic of the experimental system.

Both the peak height and the integrated absorbance measurements were recorded.

Measurements were made on-line in a continuous mode with the generator to characterize the yield of the reaction products and also in an off-line manner to trap then cryogenically (at −196 °C) for subsequent characterization *via* gas chromatography–mass spectrometry (GC–MS). A Hewlett-Packard (HP) model 6890 gas chromatograph was interfaced to an HP5973 mass selective detector (mass range 60–270 Da). Selenium compounds were separated on a 30 m × 0.25 mm i.d. × 0.25 mm film (J&W Scientific) DB1 capillary column (1% phenyl, 99% polydimethylsiloxane) using UHP helium carrier gas and a head pressure of 12.5 psi. Splitless sample injection was used. Sample aliquots of 250 μl were manually injected. The transfer line temperature was 280 °C. The carrier gas flow rate was set at 0.8 ml min^{-1}. An 18 min temperature program was used with an initial temperature of 60 °C and a hold time of 10 min followed by a ramp of 90 °C min^{-1} to a temperature of 280 °C, which was held for 10 min.

Reagents and samples

All solutions were prepared using 18 MΩ cm deionized, reverse osmosis water (DIW) obtained from a mixed bed ion-exchange system (NanoPure, model D4744, Barnstead/Thermoline, Dubuque, IA). Calibration solutions were prepared daily by diluting the stock solutions. Selenium stock solutions (1000 mg l^{-1}) were prepared from selenite (Na_2SeO_3 99%, Aldrich, USA) and selenate (Na_2SeO_4 99%, Aldrich). Solutions of formic acid (23 M, Anachemica, Canada), acetic acid (6.3 M, BDH, Canada), propionic acid (13 M, BDH) and malonic acid (BDH) were prepared from reagent-grade materials. High-purity HNO_3, $NaNO_3$ and $NaNO_2$ (Fisher Scientific) were used, except where indicated otherwise. Titania (TiNano 40 HPC-D, 99% pure) was obtained from Altair Technologies, Inc, Nevada).

Procedure

Volatile selenium compounds were generated when the selenium standard solutions containing various low molecular weight organic acids at different concentrations were pumped through the PTFE tubing of the photoreactor. In this study, sample solution irradiation times of 2 min were used.

The gaseous products were separated from the liquid in the gas–liquid separator and flushed into the heated QTA for atomic absorption spectrometry (AAS) measurements so as to determine optimal generation conditions, or passed through the successive U-tubes using a stream of helium carrier gas. Following cryocondensation, the second U-tube was closed at both ends, removed from the liquid-nitrogen bath and allowed to equilibrate to room temperature for about 15 min. A 250 μl volume of the volatile selenium species was sampled through the septum of the U-tube, using a gas-tight syringe, and injected into the chromatograph–spectrometer set-up for species identification.

RESULTS AND DISCUSSION

Based on earlier reports,[7,8] formic acid was initially investigated for its effects on the photochemical generation of volatile selenium species, as it has the simplest structure among the organic acids studied. The UV generation efficiency is dependent on the acidity under which the reaction is performed, as shown by the data in Fig. 2. In this work, 0.7 M formic acid was selected as the optimum acidity with an irradiation time of 2 min. Higher concentrations (more than 2 M) of $HCOO^-$, supplied either as formic acid or sodium formate, resulted in a decrease in signal response from volatile selenium species. By maintaining the pH < 5 with the use of H_3PO_4, a similar selenium response could be obtained when HCOONa was used as the source of formate anion. No signal was observed at pH values higher than 5.

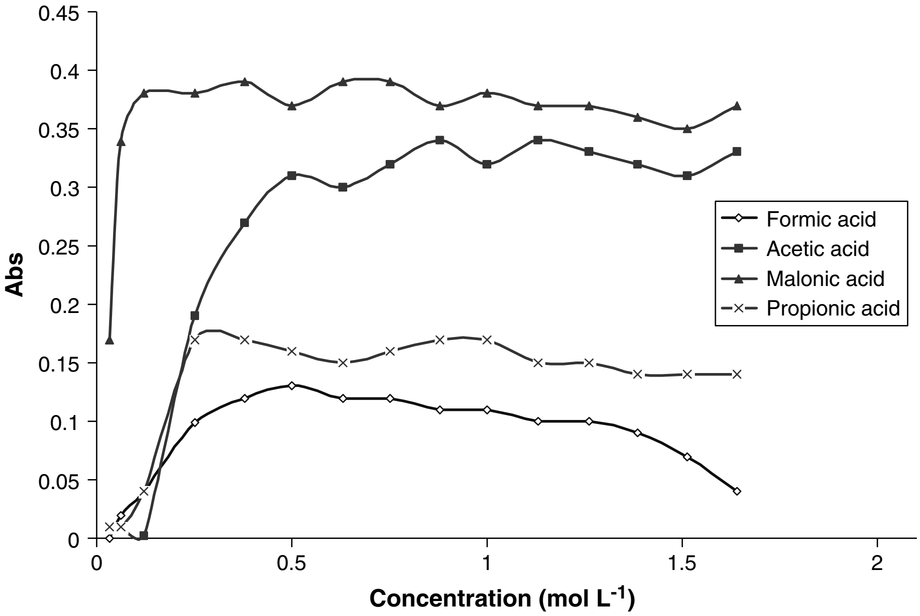

Figure 2. Effect of low molecular weight organic acid concentration on AAS signals arising from the photochemical treatment of solutions containing 0.1 mg l^{-1} selenium(IV).

Nitrate anions were found to give rise to a threefold enhancement in the yield of the volatile selenium compounds. The optimum concentration of NO_3^- depends on the concentration of formic acid used, typically 10–80 mM $NaNO_3$ for formic acid concentrations of 0.5 to 1.5 M.

Formic acid may follow either of two different pathways during its photolytic decomposition, independent of the wavelength of the absorbed radiation:[9]

$$HCOOH + h\nu \longrightarrow CO_2 + H_2 \tag{1}$$

or

$$HCOOH + h\nu \longrightarrow CO + H_2O \tag{2}$$

Reaction (1) occurs approximately sixfold more frequently than reaction (2). Although various ratios of $(CO_2 + H_2)$ to $(CO + H_2O)$ have been reported as reaction products by several independent observations,[10] hydrogen and carbon monoxide are clearly generated by these photochemical reactions. Hydrogen and carboxyl radicals generated by UV irradiation of formic acid can reduce selenite (Se^{4+}) to amorphous selenium (Se^0), as was observed in preliminary experiments, and ultimately to more volatile SeH_2 or alkyl selenide. When TiO_2 is present as a photocatalyst, production of SeH_2 has been reported.[8]

In an effort to distinguish whether SeH_2 or other carbon-bonded selenium compounds are generated in the photoreactor, the volatile species were bubbled through a solution of NaOH prior to entering the detector. It is known that SeH_2 is easily decomposed and can be completely absorbed in such an alkaline solution,[11] whereas other carbon-bonded selenium compounds are generally regarded as sufficiently stable to pass unimpeded through such a trap.[12] In this experiment, about 60–70% of the volatile selenium species was absorbed by this alkaline solution, suggesting about 60–70% SeH_2 content (*v/v*). The remaining species (30–40% *v/v*) are likely to be Se–C bonded compound(s). In the presence of 10 mM $NaNO_3$, all of the photochemical reaction products passed completely through the alkaline absorbing solution without loss, indicating that SeH_2 was no longer a product of the reaction.

The volatile selenium species resulting from this UV photosynthetic process were cryogenically trapped and identified by GC–MS. Figure 3a shows the resulting mass spectra. Based on an earlier report,[13] selenium carbonyl ($SeCO^+$ at m/z 108) has been identified. There is little information available about selenium carbonyl (SeCO) because it has only been formed in the laboratory under critical conditions and with poor yield by passing carbon monoxide over the element at 400 °C[14] or by reaction of aluminum selenide with carbonyl chloride at 219 °C.[15]

Acetic acid can also be used to generate volatile selenium compounds under UV irradiation. Increased concentration of acetate ions (as sodium acetate or acetic acid), even to the point of saturation ($[Ac^-] > 30\%$ *w/v*), produced no notable effects on the selenium signal intensity (hence product yield), provided that a slightly acidic pH of the reaction solution was maintained (i.e., pH < 5).

The NaOH trapping solution did not absorb any of the volatile reaction products. Figure 3b shows the mass spectra of the product: the molecular ion is at m/z 110, and there

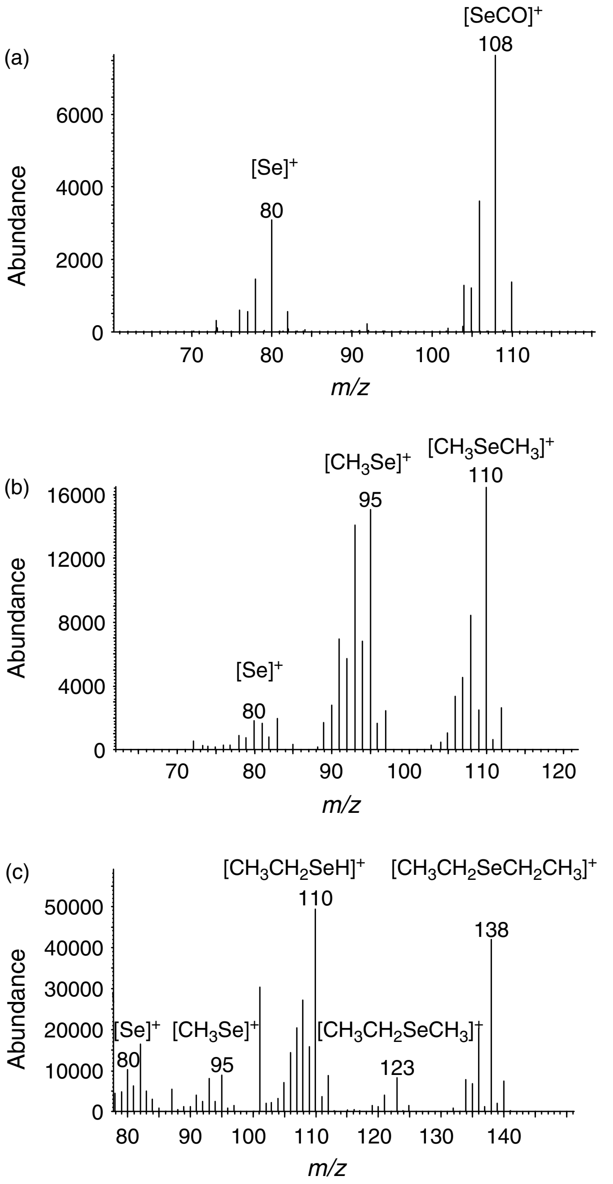

Figure 3. GC–MS spectra arising from sampling of cryogenically trapped volatile selenium compounds produced by UV irradiation of solutions containing: (a) 0.1 mg l^{-1} selenium(IV), 10 mM NaNO$_3$ and 0.7 M HCOOH; (b) 0.1 mg l^{-1} selenium(IV), 0.7 M CH$_3$COOH; (c) 0.1 mg l^{-1} selenium(IV), 0.7 M HOOCH$_2$COOH.

are fragmentation peaks at m/z 95 [CH$_3$ – Se]$^+$ and at m/z 80 [Se]$^+$. It may be concluded that the volatile selenium-containing species produced by UV photolysis of selenite in acetic acid solution is dimethylselenide, (CH$_3$)$_2$Se.

In addition to acetic acid, dimethylselenide could also be generated from a malonic acid solution. A chromatogram and a mass spectrum illustrating the composition of the products are shown in Fig. 3c. The conditions for generation of dimethylselenide from a malonic acid medium are very similar to those used with acetic acid (cf. Fig. 2). This might be attributable to the $^{\bullet}$CH$_2$COOH radical, acetic acid, as well as CO$_2$ produced by UV irradiation.[16] With malonic acid, a higher yield of dimethylselenide was obtained and a shorter irradiation time could be used compared with conditions arising from the use of acetic acid.

The photochemical methylation yield was estimated from a comparison of the resulting AAS signals with those arising from conventional generation of SeH$_2$ using a classical NaBH$_4$–HCl hydride-generation system. More than 50% of the inorganic selenium was transformed to volatile dimethylselenide in the malonic acid solution using a 2 min UV irradiation. A similar yield was obtained in an acetic acid generation medium.

UV irradiation of a propionic acid solution containing inorganic selenium also resulted in the generation of a volatile selenium-containing product (cf. Fig. 2); its mass spectrum is presented in Fig. 3c. A molecular ion at m/z 138 [CH$_3$CH$_2$ – Se – CH$_2$CH$_3$]$^+$, and several fragmentation peaks at m/z 123 [CH$_3$CH$_2$ – Se – CH$_2$]$^+$, m/z 110 [CH$_3$CH$_2$ – SeH]$^+$, m/z 95 [CH$_3$ – Se]$^+$, m/z 82 [SeH$_2$]$^+$ and at m/z 80 [Se]$^+$ are evident and are consistent with the reported mass spectrum of diethylselenide (DESe). It is clear that the volatile selenium-containing species produced by UV photolysis of selenite in propionic acid solution is diethylselenide (CH$_3$CH$_2$)$_2$Se.

The effect of temperature on the reaction yield was studied. The sample solution (Se^{4+}, 0.1 mg l^{-1}) was kept in either an NaCl ice bath (−3 °C) or a hot-water bath (80 °C) prior to sampling. No effect of temperature on the response was observed. Further investigations were done in an effort to distinguish photochemical effects from 'thermal' effects. When the UV lamp was covered with a thin sheet of aluminum foil placed between it and the PTFE reactor tubing, the thermal effect was still present whereas UV irradiation of the sample was prohibited. In such a case, volatile selenium species were no longer formed.

Although the detailed reaction sequence is still unclear, based on the results obtained above, the following simplified general reaction may occur:

$$\begin{gathered} 2\text{RCOOH} + \text{Se(IV)} + h\nu \longrightarrow \text{R}_2\text{Se} \uparrow + 2\text{CO}_2 + \text{H}_2 \\ (\text{R} = \text{C}_n\text{H}_{2n+1}, n = 0, 1, 2) \end{gathered} \tag{3}$$

wherein the bond between the α-carbon and the carboxyl group is severed. The energy required to break the C–C bond is 84 kcal mol^{-1}; breaking the C–OH bond requires 90 kcal mol^{-1}.[17] These energies are equivalent to UV wavelengths of 341 nm and 316 nm, respectively.

CONCLUSIONS

These studies have demonstrated that inorganic selenium can be easily converted into an organic form by the action of UV light, thereby providing a novel means of synthesizing/vaporizing organoselenium compounds in high yield.[18] Some of our initial results (not presented) imply that a similar process may occur for a number of other metal(oid) elements.

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