DEVELOPMENT OF A PORTABLE HYDROGEN IODIDE GENERATOR

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ABSTRACT

Because the ban on chlorofluorocarbcns has been revised to include Halon 1301 and Halon 1211, the two main fire suppression reagents used in armored vehicles. the search is on for alternative fire extinguishing reagents with the desirabie properties of Halons 1301 and 1211. Trifluoroiodomethane had been the most promising replacement reagent, but it has recentiy failed critical toxicity tests. Nevertheless, it is likely that the better candidates for fire extinguishing reagents that are used to flood contained spaces wiil be found among the iodine containing fluorocarbons. All halogenatsd hydrocarbons form hydrogen halides, as toxic by-products, during fire suppression, and the real time monitoring of these by-products in dispersion clouds is criticai. Portable analyzers are being developed for this purpose. and such analyzers require calibration. At present. there is no commercial source of hydroqen icdide gas, which is needed to calibrate the hydrogen iodide gas anaiyzer. In this paper. the design and characrerization of laboratory bench chemical and photochemical hydrogen iodide gas generators, wnich show tne greatest promise for scaie-down to portable units, are presented. Based on the yield of hydrogen iodide gas, the bese cnemicai qenerator is based on the metathesis reaction between potassium iodide and orthophoshoric acid. Preliminary results suggest that a pcrtable pnotochemicai generator based on methyiodide may also be feasible.

INTRODUCTION

Halon 1301 (**CBrF$_3$**) and Halon 1211 (**CBrClF$_2$**) are currently the two main fire suppression reagents used in armored vehicles, such as tanks. At 6 volume%, these halons are not directly toxic to animals or humans [1-5]. However, toxic by-products, such as $HF_{(g)}$, $HCl_{(g)}$ and $HBr_{(g)}$, are produced during fire suppression; these gases constitute a localized hazard. By measuring their spatial and temporal profiles, one can obtain information needed to minimize the impact of the hazard. For this reason, portable analyzers for the real-time monitoring of these gases have been under development at the U.S. Army Center for Health Promotion and Preventive Medicine at Fort Detrick. In addition to tropospheric toxic gases, Halon 1301 produces stratospheric bromine radicals and Halon 1211 produces both stratospheric bromine and stratospheric chlorine radicals. Both types of radicals are ozone depletion agents, so that Halon 1301 and Halon 1211 are effectively indirect, globally toxic substances. Under the revised Montreal Protocol on Substances That Deplete the Ozone Layer, their manufacture was banned on January 1, 1994. Much research is being done to find a suitable replacement. Trifluoroiodomethane became a strong candidate in 1994, but it has recently failed several toxicity tests. Still, it is likely that a successful candidate will be found among hydrocarbons containing fluorine and iodine. The development of a portable HI$_{(g)}$ anaiyzer is anticipatory to such an eventuality.

One of the most critical steps in an instrumental measurement is the calibration step. The portable $HX_{(g)}$, X = F. Cl, Br or I. anaiyzers require gas mixtures with known amounts of HF, HCl, HBr or HI. Gas mixtures of HF, HCl, or HBr in Ar, He or N_2 are commercially available. However, neither $HI_{(g)}$ or gas mixtures of HI in Ar, He or N_2 are commercially available. For greatest accuracy, the calibration steps need to be juxtaposed to the measurement steps. This requires portability, which is achieved by means of lecture bottle gas mixtures for commercially available gases. It is evident that a portabie HI$_{(g)}$ generator is needed for

the calibration of the portable $HI_{(g)}$ analyzer.

The development *of* a portable $HI_{(g)}$ generator is evolvina in three stages -- 1. design and characterization of laboratory bench $HI_{(g)}$ generators, **2.** scale-down and modification to achieve portability, and 3. field testing of portable units. In this paper, the temporal yield behavior and the overall yield for three chemical laboratory bench $HI_{(g)}$ generators and one photochemical laboratory bench $HI_{(g)}$ generator are discussed. Based on these results, a design for a portable HI_{g} generator will be presented.

HI GENERATION: CHEMICAL AND PHOTOCHEMICAL CONSIDERATIONS

The catalytic union of the elements is a well established method for HI generation. as shown in Figure 1 [6]. This method is predominantly used to prepare aqueous solutions of HI, but by eliminating the gas adsorption vessel, **a** mixture of $HI_{(g)}$ ana $H_{2(g)}$ will be obtained. This method is not conducive to portability. because the catalyst tube must be heated to about 500^3 C and constant monitorinq to prevent iodine from condensina in and plugging the cooling coil region is needed.

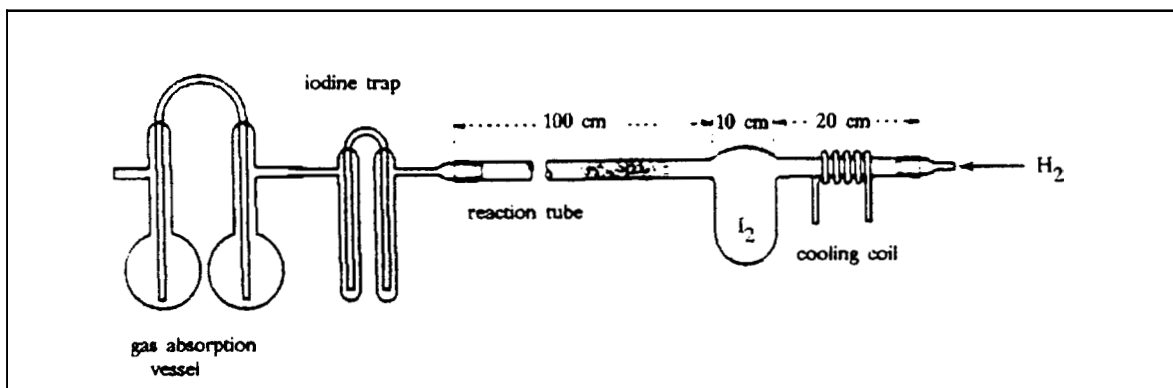Figure 1. Hydrogen iodide generation by catalytic union of the elements.

Rollefson and Booher [7] prepared $HI_{(g)}$ by dehydrating hydriodic acid with phosphorus pentoxide. The gas evolved was passed through a tube of phosphorus pentoxide and then condensed in

a tube containing mercury coated walls. This latter distillation process was repeated **4** times. Provided that the solid state distillation process can be eliminated, dehydration of hydriodic acid is a simple reaction for which portability can be achieved.

Stone and Shechter [8] described an in-situ method of generating HI for organic syntheses. In particular, they reacted cyclohexene, potassium iodide and *95%* orthophosphoric acid to obtain iodocyclohexane and potassium dihydrogen phosphate. A note by the authors, "The solution should be cooled to room temperature before addition of potassium iodide; otherwise evolution of hydrogen iodide and formation of iodine will take place." suggested that $HI_{(g)}$ could be produced in the absence of organic substrate.

The chemical generators have two foreseeable major disadvantages. Firstly, they are messy. The apparatus will have to be completely disassembled and cleaned after each use. Secondly, they are discrete generators, i.e. they produce HI,,,over a short time interval determined by the reaction kinetics. Photochemical generation of $HI_{(g)}$ has the potential of overcoming these disadvantages. The use of a liquid reactant with a boiling point less than 100° C would be particularly advantageous. The reactant could be added to the reaction vessel by means of an addition funnel, and volatilized into the gas phase by means of a boiiing water bath. Gas generation would occur continuously up to a time determined by the capacity of the addition funnel. With judicious choice of the reactant, most of the products will be gases; only iodine would crystallize into a solid, but the apparatus could be cleaned by volatilizing it with a heat gun.

Recent studies on 2-iodopropane suggested to us that it might be a good reactant. It is a liquid with a boiling point of 90° C. Irradiation at 248 nm causes a transition of a lone pair electron on the iodine atom of the ground state molecule (N) into a σ^* bond localized mostly on the C-I bond of the $^3Q_3$ excited state [9]. Since rapid dissociation to an isopropyl radical and an iodine atom occurs, with the intermediates having parallel unpaired electrons, recombination is not favored and a photofragmentation quantum yield of 1 is realized. Furthermore, irradiation of 2-iodopropane with

248 nm light also leads to substantial **H** atom production [10]; so we postulated that **I** and **I**' atoms and **H** atoms would react with ground state 2-iodopropane molecules to produce mainly $HI_{(g)}$ and $I_{2(g)}$ by iodine atom abstraction, the energy of reaction being deposited in the isopropyl radical left behind. We could find no paper giving the complete profile for products and their yields under photochemical conditions. Nevertheless, with respect to iodine, the main forms should be HI,,, $I_{2(g)}$ and unreacted 2-iodopropans. By using a cooling column, unreacted 2-iodopropane can be returned to the reaction flask, while $I_{2(g)}$ will deposit as the solid.

EXPERIMENTAL

Chemical generator **I** was based on the dehydration of hydriodic acid using phosphorus pentoxide. The apparatus is shown in Figure 2. Hydriodic acid (Matheson Coleman & Bell, 57%, Reagent Grade) is placed in the addition funnel without further purification, and it is added with stirring to phosphorus pentoxide (99.8%, Fisher Scientific Company) in the three-flask. The cooling column is water cooled. Both reagents were obtained from chemical scores, but it was obvious that the hydriodic acid was impure, since it was orangish-brown in color. One of the impurities is iodine, as demonstrated by carbon tetrachloride extraction. The actual amount of hydriodic acid in the reagent was determined **by** titration with sodium hydroxide.

Chemical generator II is based on the metathesis reaction *of* KI and orthopnosporic acid using the procedure of Stone and Shechter. In this procedure, 85% orthophosphoric acid (Fisher Scientific Company, **A.C.S.** Certified) is added to phosphorus pentoxide to form 95% orthophosphoric acid. The solution is cooled to room temperature, and potassium iodide (Fisher Scientific Company, A.C.S. Certified) **is** added with stirring. The addition funnel in Figure 2 is replaced by a glass stopper. Chemical generator III is based on the same metathesis reaction, but now potassium iodide is placed in the reaction flask, and 85% orthophosphoric acid is added by means of the addition funnel. We

also mixed potassium iodide with phosphorus pentoxide in the reaction flask, and added 85% orthophosphoric acid via the addition funnel. Finally, we reacted **85%** orthophosphoric acid with phosphorus pentoxide to get 95% orthophosphoric acid. The latter was placed in the addition funnel and added to potassium iodide in the flask.
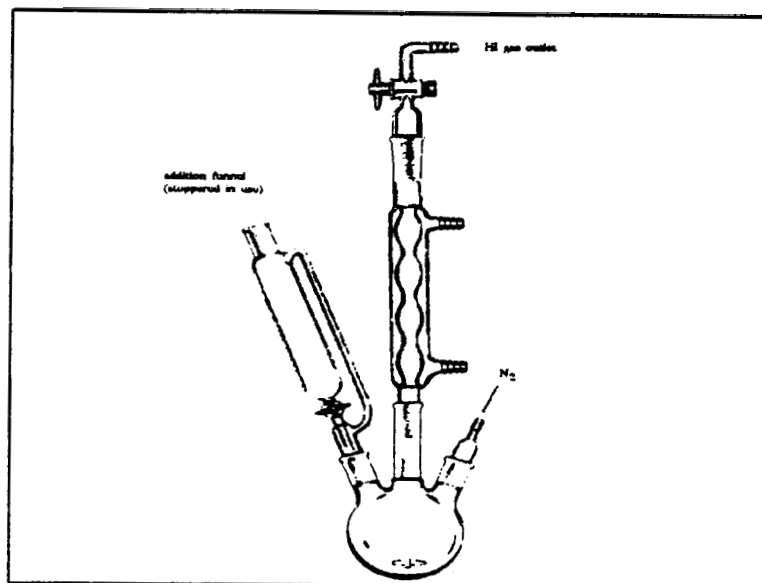

Figure 2. Basic apparatus for chemical generation of $HI_{(g)}$.

For the photochemical generator, the apparatus has been slightly modified to allow for the insertion of a Spectroline shortwave UV pencil lamp **(254** nm, 4500 $\mu W\ cm^{-2}$ at 1 in distance, Fisher Scientific Company), as shown in Figure **3.** 2-iodopropane (99%, Aldrieh Chemical Company) was added dropwise from the addition funnel. Photolysis was performed using continuous irradiation, intermittent irradiation and pulse irradiation at . 0^{0} C, room temperature or **62**^{0} C.

In all cases, the gas escaping from the generator outlet was passed through a section of fluram fluoroelastomer tubing (Fisher Scientific Company) and bubbled into an electrochemical cell consisting of a Corning iodide/cyanide ion selective electrode (ISE), a double junction silver chloride reference electrode and 250 mL of 0.2 F potassium nitrate (A.C.S. Certified.. Fisher Scientific Company). Prior to running the first **gas** generation

experiment, the cell calibration curve was obtained at constant ionic strength. The curve was linear with a slope factor of 55.3 mV per decade on a concentration range of 10^{-5} to 10^{-2} mol L^{-1} of iodide. E_{cell} was measured using an Accumet 750 Ion Selective Analyzer (Fisher Scientific Company) interfaced to a 286-12 MHz compatible microcomputer (GoldStar) by means of a PCL812G analog/digital 1/0 board (Advantech Co., Ltd.). Data collection is performed under computer control using a program written by one of the authors (VY). Percent yield was calculated as follows:

$$\%yield = \frac{antilog[\dfrac{322+E_f}{-55.3}] - antilog[\dfrac{322+E_i}{-55.3}]}{C_{theor}} \cdot 100\%$$

where E_f is the final cell emf, E_i is the initial cell emf, and C_{theor} is the theoretical concentration based on the amount of the limiting reagent.
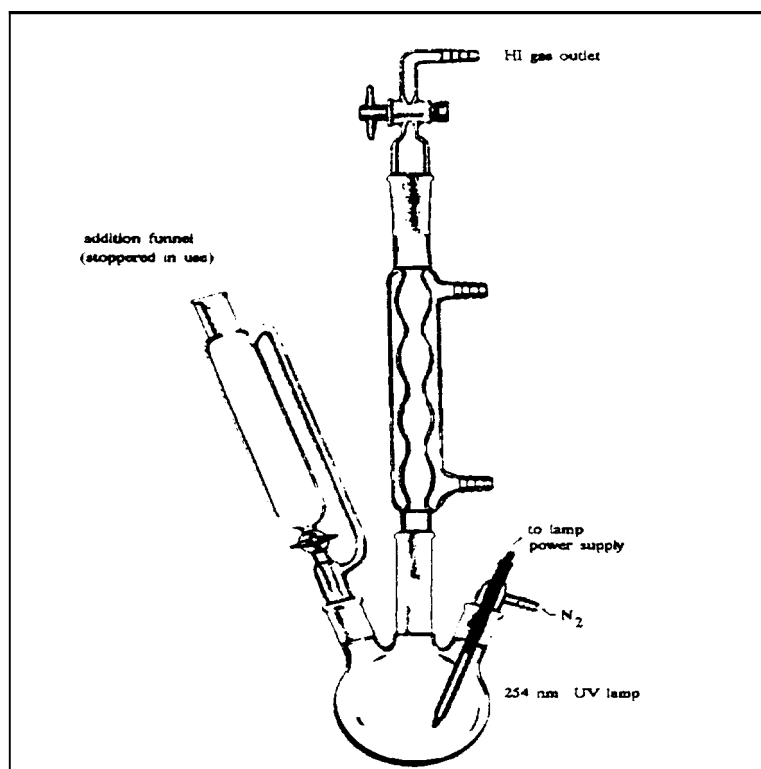

Figure 3. Apparatus for photochemical $HI_{(g)}$ generation.

RESULTS

Generation of $HI_{(g)}$ by dehydration of hydriodic acid is attractive, because of its apparent simplicity. However, we abandoned this procedure after only three experiments --- two without cooling and one with cooling the reaction flask. In the latter case, the yield of HI,,, based on the actual amount of hydriodic acid in the starting reagent is only **0.37%**. This suggests that the starting hydriodic acid must be very pure, because iodine probably enhances decomposition of HI ,.. Commercial hydriodic acid would have to be distilled before use, which makes the procedure less attractive.

Generation of HI,? by the metathesis between potassium iodide and orthophosphoric acid works quite well. We began with experiments based on chemical generator III; and because we were able to adjust conditions so as to achieve high yields, we did not do experiments based on chemical generator II. When 85% orthophosporic acid is added to potassium iodide without cooling and the nitrogen gas is flowed to collect the products. no $HI_{(g)}$ is detected. When 85% orthophosphoric acid is added to a mixture of potassium iodide and phosphorus pentoxide and the nitrogen gas is flowed to collect the products, a HI,! yield of 4.2% is obtained. If the flow of nitrogen gas is begun before the addition of the acid, the yield increases to 107%. We repeated the experiment after thoroughly washing the fluram tubing, and got a yield of **81%**. This shows that HI,,, adsorbs on this extremely inert tubing, so that carry over occurs, if the tubing is not cleaned between experiments. **A** lot of heat is generated in these reactions, which we concluded was mainly due to the reaction between phosphoric acid and phosphorus pentcxide. Consequently, we generated 95% orthophosphoric acid by reacting the 85% acid with phosphorus pentoxide, and then placed that in the addition funnel. The reaction time increased, but so did the yield -- to a calculated value of 145%. This value is based on the potential change of the raw signal, which is significantly distorted by instrument drift. We repeated the experiment without cleaning the tubing. and got a
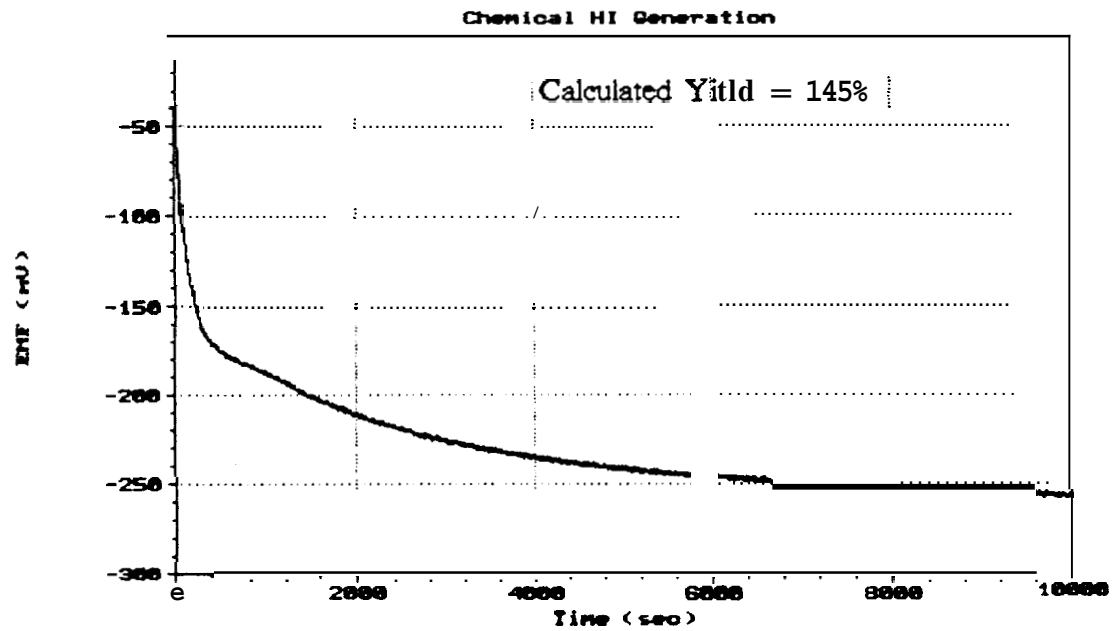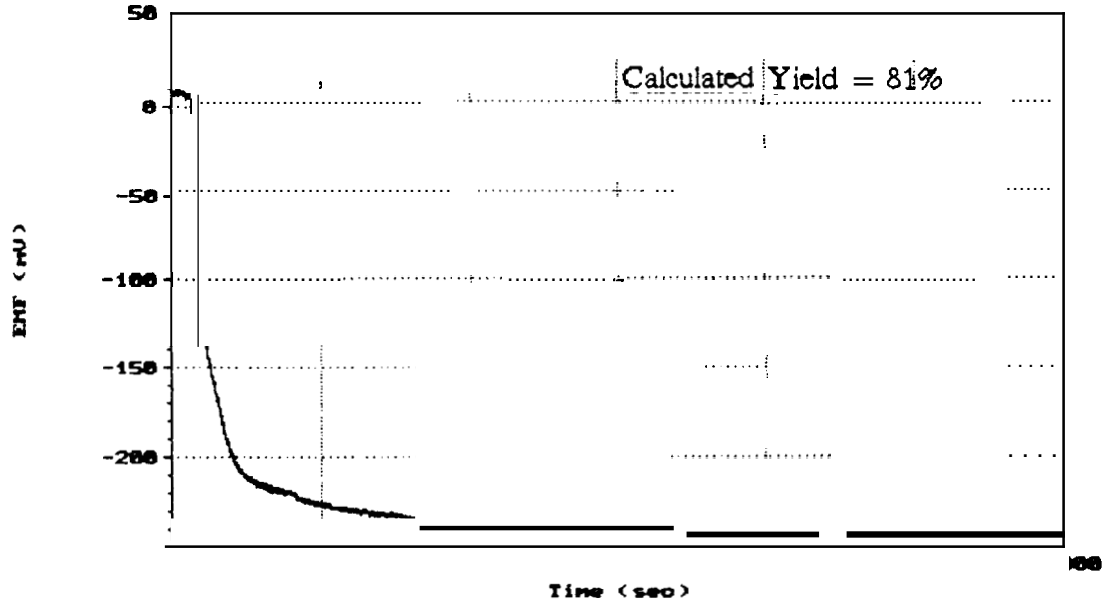
Chemical HI Generation

Figure 4. Examples of time dependent signals for $HI_{(g)}$ generation using Chemical Generator III.

calculated yield of 185%. Clearly, yields in excess of 81% arepossible using this generator. It represents the best chemical generator design of those studied, and it can easily be made portable. Examples of the signal time evolution curves are shown

in Figure 4. It is evident that such a calibration source must be "sniffed" over a finite time interval on the steeply changing portion of the curve.
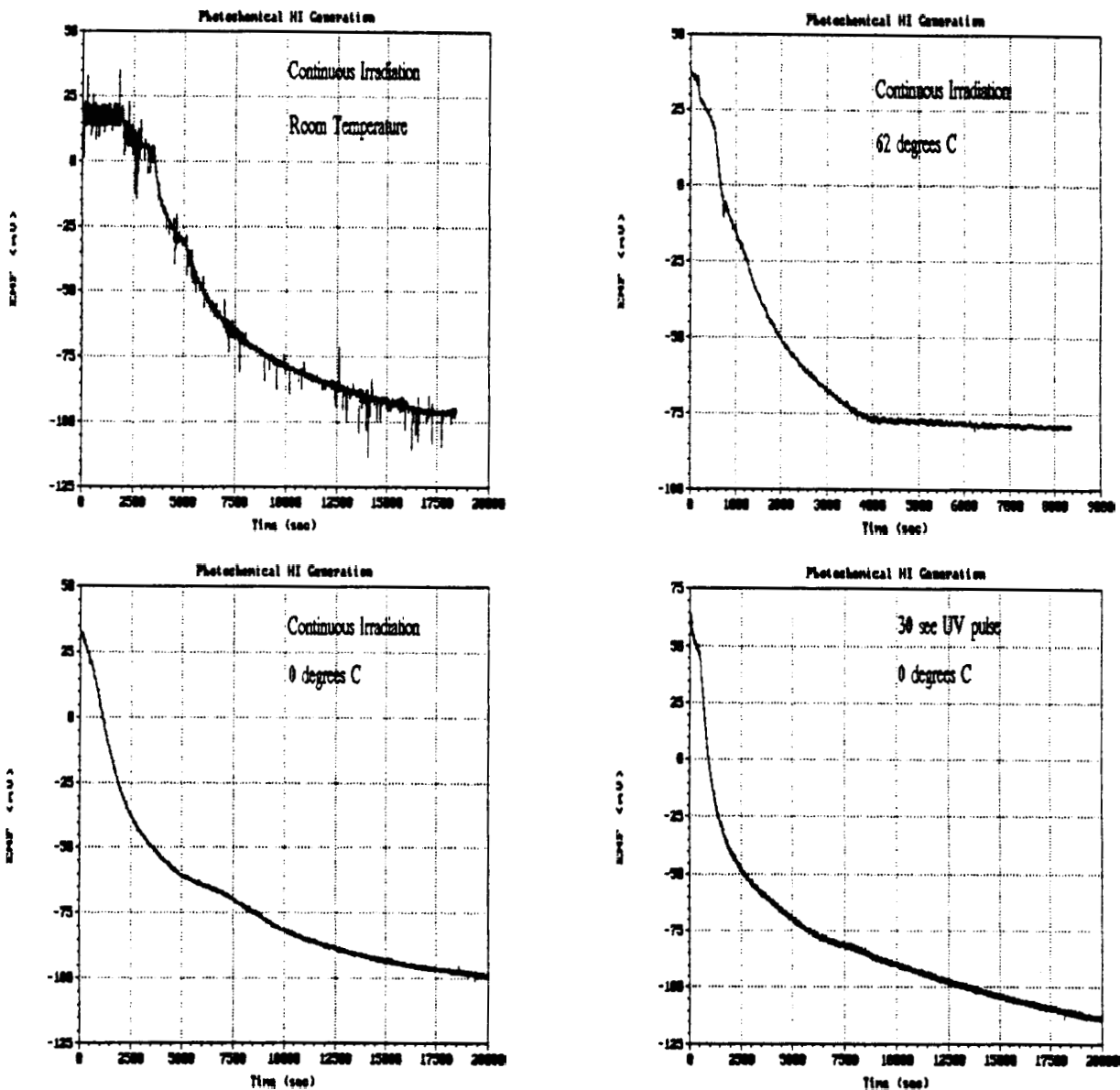

Figure 5. Examples of time dependent signals for photochemical generation of HI,,,using 2-iodopropane.

For photochemical generation using **2-3** mL of 2-iodopropane, yields of $HI_{(g)}$ ranged from a minimum of 0.01% (for a 30 second UV pulse and room temperature) to a maximum of 0.06% (for a 30 secondUV pulse and 0° C). For continuous irradiation, the yield of

$HI_{(g)}$ was 0.04% at 0^0 C, 0.05% at room temperature and 0.03% at 62" C.

Examples of the signal time evolution curves are shown in Figure 5. Using cur yield results, we calculated the cost (based on reagent prices) to produce 33.6 L of $HI_{(g)}$ at STP for each method as follows: $18,070 for dehydration of hydriodic acid (0.37% yield), $257 for metathesis **of** potassium iodide and orthophosphoric acid (90% yield) and $39,100 for photochemical generation from 2-iodopropane (0.06% yield). When 2-iodopropane is used as the reactant, the convenience of photochemical generation is nsgated by the cost. Also, a prolonged "sniff" by the analyzer would be needed to obtain an adequate standard concentration. With a yield of 1%, the cost would be only 10 times that of chemical generation based on the metathesis reaction. In such a case, the benefits would outweigh the costs. We have very preliminary results that indicate that HI,, yields in excess of 1% can be achieved using methyl iodide as the photochemical reactant.

CONCLUSIONS

it is definitely possible to build a portable $HI_{(g)}$ generator based on the metathesis reaction of potassium iodide and orthophosphoric acid. Lecture bottle nitrogen can be used as the carrier gas in the system. The Alihn condenser would have to be replaced by a Dewar condenser, which would be loaded with ice. If further experiments confirm the preliminary photochemical results obtained with methyl iodide, then a portable photcchemical HI,, generator becomes feasible. It will be necessary to build a battery operated power supply for the UV lamp, in addition to adding lecture bottle nitrogen and switching from an Alihn condenser to a Dewar condenser. The unit can be housed in a carrying case. and the overall weight **will** be less than 20 lb.

The findings in this report are not to be construed as an official Department of the Army position uniess so designated by other authorized documents.

ACKNOWLEDGMENT

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