DEVELOPMENT OF A PORTABLE HYDROGEN IODIDE GENERATOR

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ABSTRACT

Because the ban on chlorofluorocarbons 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 desirable properties of Halons 1301 and 1211. Trifluoroiodomethane had been the most promising replacement reagent, but it has recently failed critical toxicity tests. Nevertheless, it is likely that the better candidates for fire extinguishing reagents that are used to flood contained spaces will be found among the iodine containing fluorocarbons. All halogenated hydrocarbons form hydrogen halides, as toxic by-products, during fire suppression, and the real time monitoring of these by-products in dispersion clouds is critical. Portable analyzers are being developed for this purpose, and such analyzers require calibration. At present, there is no commercial source of hydrogen iodide gas, which is needed to calibrate the hydrogen iodide gas analyzer. In this paper, the design and characterization of laboratory bench chemical and photochemical hydrogen iodide gas generators, which show the greatest promise for scale-down to portable units, are presented. Based on the yield of hydrogen iodide gas, the best chemical generator is based on the metathesis reaction between potassium iodide and orthophosphoric acid. Preliminary results suggest that a portable photochemical generator based on methyliodide may also be feasible.
INTRODUCTION

Halon 1301 (CBrF₃) and Halon 1211 (CBrClF₃) 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 HF₃, HCl₃, and HBr₃, 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. Trifluorooiodomethane 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 HI₃ analyzer is anticipatory to such an eventuality.

One of the most critical steps in an instrumental measurement is the calibration step. The portable HX₃, X = F, Cl, Br or I, analyzers require gas mixtures with known amounts of HF, HCl, HBr or HI. Gas mixtures of HF, HCl, or HBr in Ar, He or N₂ are commercially available. However, neither HI₃ or gas mixtures of HI in Ar, He or N₂ 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 portable HI₃ generator is needed for
the calibration of the portable HI \(_4\) analyzer.

The development of a portable HI \(_4\) generator is evolving in three stages -- 1. design and characterization of laboratory bench HI \(_4\) 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 \(_4\) generators and one photochemical laboratory bench HI \(_4\) generator are discussed. Based on these results, a design for a portable HI \(_4\) 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, ana HI \(_4\) will be obtained. This method is not conducive to portability because the catalyst tube must be heated to about 500\(^\circ\) C and constant monitoring to prevent iodine from condensing 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, 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 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 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 boiling 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 1Q 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 \cite{10}; so we postulated that I and I' atoms and H atoms would react with ground state 2-iodopropane molecules to produce mainly HI\(_{2}\) and I\(_{2}\) 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\(_{2}\), I\(_{2}\), and unreacted 2-iodopropanes. By using a cooling column, unreacted 2-iodopropane can be returned to the reaction flask, while I\(_{2}\) 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 orthophosphoric 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 35\% 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 µW cm$^{-2}$ at 1 in distance, Fisher Scientific Company), as shown in Figure 3. 2-iodopropane (99%, Aldrich Chemical Company) was added dropwise from the addition funnel. Photolysis was performed using continuous irradiation, intermittent irradiation and pulse irradiation at 0$^\circ$ C, room temperature or 62$^\circ$ 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 $10^{-1}$ to $10^{-1}$ mol L$^{-1}$ of iodide. $E_{\text{cell}}$ 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:

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

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

Figure 3. Apparatus for photochemical HI$_2$ generation.
RESULTS

Generation of $\text{HI}_{(g)}$ 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 $\text{HI}_{(g)}$, 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 $\text{HI}_{(g)}$. Commercial hydriodic acid would have to be distilled before use, which makes the procedure less attractive.

Generation of $\text{HI}_{(g)}$ 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% orthophosphoric acid is added to potassium iodide without cooling and the nitrogen gas is flowed to collect the products, no $\text{HI}_{(g)}$ 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 $\text{HI}_{(g)}$ 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 $\text{HI}_{(g)}$ 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 pentoxide. 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
Figure 4. Examples of time dependent signals for HI\textsubscript{1;1} generation using Chemical Generator III.

calculated yield of 185%. Clearly, yields in excess of 81% are possible 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.

![Graphs showing time dependent signals for photochemical generation of HI, using 2-iodopropane.](image)

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 were from a minimum of 0.01% (for a 30 second UV pulse and room temperature) to a maximum of 0.06% (for a 30 second UV pulse and 0°C). For continuous irradiation, the yield of
HI$_2$ was 0.04% at 0°C, 0.05% at room temperature and 0.03% at 62°F.

Examples of the signal time evolution curves are shown in Figure 5. Using our yield results, we calculated the cost (based on reagent prices) to produce 33.6 L of HI$_2$ 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 $39,100 for photochemical generation from 2-iodopropane (0.06% yield). When 2-iodopropane is used as the reactant, the convenience of photochemical generation is negated by the cost. Also, a prolonged "sniff" by the analyzer would be needed to obtain an adequate standard concentration. With a yield of 1%, the cost would be only 10 times that of chemical generation based on the metathesis reaction. In such a case, the benefits would outweigh the costs. We have very preliminary results that indicate that HI$_2$, 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$_2$ 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 photochemical HI$_2$, 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 unless so designated by other authorized documents.
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REFERENCES

2. D.G. Clark, ibid, p. 60-69.