

# Photochemical hydrogen iodide gas generation from iodomethane and 2-iodopropane

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## Abstract

The photochemistry of iodomethane has been widely studied, but quantitative product yields for hydrogen iodide gas have not been reported. The photochemistry of 2-iodopropane has not been as widely studied, but it has been reported that trace amounts of hydrogen iodide gas are formed. However, quantitative product yields for hydrogen iodide gas have not been reported for this reactant either. In this paper, we report results for the percentage yields of hydrogen iodide gas, as obtained by potentiometry, when iodomethane or 2-iodopropane are photolyzed at 253.7 nm. For iodomethane, the statistical most likely estimator is  $3.8 \times 10^{-3}\%$ , and the set maximum is 0.049%. For 2-iodopropane, the statistical most likely estimator is 0.26%, and the set maximum is 3.68%. © 1998 Elsevier Science S.A. All rights reserved.

**Keywords:** Photochemistry; Hydrogen iodide gas generation; Iodomethane; 2-iodopropane

## 1. Introduction

The development of a portable gas analyzer for the real-time spatial and temporal monitoring of hydrogen iodide gas (HI) has created a need for an on-demand source of HI, which is not availability commercially. Because of the sensitivity of the gas analyzer's detector, the generation does not have to be efficient. More important are a steady output of HI, the ability to achieve portability and the simplicity of clean up. Photochemical HI generation has the potential to satisfy these latter criteria, particularly if the reactant is a low molecular weight iodoalkane.

Iodomethane has been extensively studied recently because of its use in the first photodissociation laser [1]. The lasing results from a photochemical product,  $I^*(^2P_{1/2})$ , which is produced in the first primary channel,



The primary quantum yield for this process is approximately 1 at 253.7 nm [2]. By trapping methylene using various additives, Takacs and Willard [3] have determined an upper bound for the primary quantum yield of the channel



They determined a value of  $\Phi_{\text{methylene}} \leq 5 \times 10^{-5}$ , which is

also an upper bound for the primary quantum yield of HI. None of the researchers cited in Ref. [2] report HI among the products formed for the photolysis of iodomethane at 253.7 nm. Some of the experiments were not designed to detect HI, e.g., West and Schlessinger [4] collected products volatile at  $-180^\circ\text{C}$ , products volatile at  $-80^\circ\text{C}$  and then examined the residue at room temperature. HI would have been lost, since it boils at  $-35.38^\circ\text{C}$ . Emschwiller [5] also studied this photochemical reaction and looked for HI, but found none. The following secondary process could produce HI:



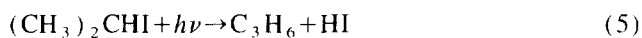
However, this is a low probability pathway, since the following collision process is more probable:



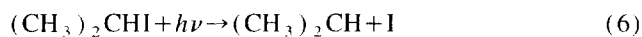
Since no quantitative product yields have been reported for HI produced by photolysis of iodomethane, we have examined its production in this work. The photolysis of iodomethane is not expected to be useful for HI generation, but the reaction is useful in assessing the sensitivity of our detection system.

The primary photochemical channels for 2-iodopropane are the same as those for iodomethane, with one important difference: the primary quantum yield for the channel

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is  $\leq 0.1$  at 313.0 nm [6]. Emschwiller [5] reported that traces of HI were formed by the photolysis of 2-iodopropane using 253.7 nm radiation, but no quantitative data was provided. McMillan and Noyes [7], who studied this reaction at 313.0 nm, also provided no quantitative results for HI, but stated emphatically that it must form. McCauley et al. [8] qualitatively tested for the presence of HI as an intermediate in the photolysis of iodopropane and 2-iodopropane, but provided no quantitative data. The channel



leads to copious amounts of iodine atoms. Unlike iodomethane, photolysis of 2-iodopropane also leads to substantial hydrogen atom production [9]. Thus, some HI should be produced by means of the secondary reaction



where M is some molecule, in the reaction vessel, which acts as a third body. Thus, photolysis of 2-iodopropane is potentially useful as a source of HI, and we also report here results for the product yields of HI produced by the photolysis of 2-iodopropane at 253.7 nm.

## 2. Experimental

The experimental setup consists of two modules, the photochemical generator (Fig. 1) and the HI monitoring system (Fig. 2). The photochemical generator consists of a 250 ml 3-neck flask, a thermometer inlet adapter with gas inlet, a thermometer with range  $-20^\circ\text{C}$  to  $150^\circ\text{C}$ , a Spectroline pencil UV lamp (11 SC-1, 253.7 nm,  $4500 \mu\text{W cm}^{-2}$ ) seated by means of a specially machined inlet adapter, a 200 ml capacity Dewar condenser, and a glass valved gas outlet. A special insulation jacket fabricated from fiberglass and plastic pipe wrap insulation has been made for the Dewar condenser. A potentiometric monitoring system is used. The electrochemical cell contains a temperature compensation probe, a double junction Ag/AgCl reference electrode (Corning 476370), either a pH electrode (Corning 476281 or Fisher 13-620-256) or a  $\text{I}^-/\text{CN}^-$  ion selective electrode (ISE) (Corning 476127) and 100 ml of a solution which is 0.10 M in potassium nitrate and either  $5.0 \times 10^{-6}$  M or  $1.0 \times 10^{-6}$  M in potassium iodide. The  $\text{I}^-/\text{CN}^-$  electrode is used to measure the iodide produced as a result of the dissociation



The pH electrode is used to measure the hydronium ion produced by reaction (8), since some  $\text{I}^-$  might be present as triiodide, due to the equilibrium [10]



This reaction will occur if some of the iodine produced in the reaction flask makes it to the electrochemical cell. The  $\text{I}^-/$

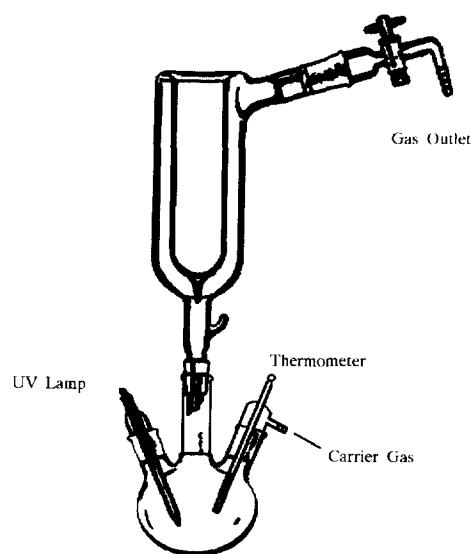


Fig. 1. Photochemical HI gas generator. Insulation jacket and lamp power supply not shown.

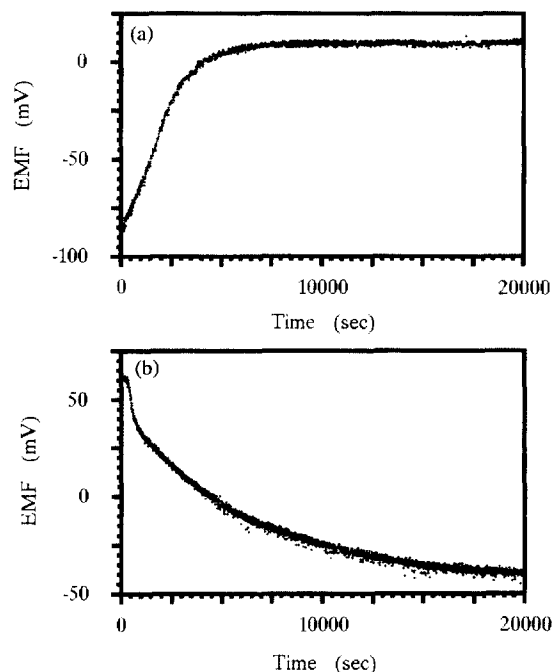


Fig. 2. Temporal  $\text{H}_3\text{O}^+$  curve (a) and temporal I curve (b) for iodomethane photolysis. Condenser temperature  $-11^\circ\text{C}$ .

$\text{CN}^-$  electrode cannot see triiodide. If the iodine produced is trapped in the Dewar with 100% efficiency, than hydronium ion monitoring and iodide ion monitoring will give statistically identical results.

The temporal cell potential is measured by a Fisher Accumet Model 750 Selective Ion analyzer interfaced to either a 286-12 MHz or 386-20 MHz PC compatible by means of a PCL812PG analog/digital input/output board. The output of the photochemical generator is delivered to the electrochemical cell by means of fluoroelastomer Fluram tubing, terminated with an in-house machined teflon tip.

Volatile products are swept out of the reaction flask using nitrogen gas. The flow rate is determined qualitatively in terms of bubbles  $\text{min}^{-1}$  exiting the teflon tip. The Dewar condenser is filled with ice ( $0^\circ\text{C}$ ) or ice mixed with rock salt. In the latter case, the temperature is monitored with a thermocouple probe and a LCD digital multimeter (Radio Shack 22-174A). The pH electrodes are calibrated using certified Fisher buffer solutions ( $\text{pH}=4.00\pm 0.01$ ,  $\text{pH}=7.00\pm 0.01$  and  $\text{pH}=10.00\pm 0.02$ ). The slope factors are  $-56.9\text{ mV decade}^{-1}$  for the Corning electrode and  $-56.9\text{ mV decade}^{-1}$  for the Fisher electrode. The  $\text{I}^-/\text{CN}^-$  ISE is calibrated using a set of standards with  $[\text{I}^-]=1.0\times 10^{-2}\text{ M}$ ,  $1.0\times 10^{-3}\text{ M}$ ,  $1.0\times 10^{-4}\text{ M}$ ,  $1.0\times 10^{-5}\text{ M}$  and  $1.0\times 10^{-6}\text{ M}$ , all with ionic strength  $\mu=0.10\text{ M}$ . The electrode had a slope factor of  $63.0\text{ mV decade}^{-1}$  when new, and with time it degraded to  $51.9\text{ mV decade}^{-1}$ . All data are collected under computer control using a program written by one of the authors.

An experiment consists of loading the Dewar condenser, turning on the nitrogen gas and measuring the flow rate, monitoring the Accumet display until the cell potential reading is constant, and then adding 3.0 ml of iodomethane or 2-iodopropane to the reaction flask. Data collection is started and the UV lamp is turned on. The reaction is run until no reactant remains in the flask. The percent yield is calculated using the following equation:

$$\% \text{YIELD} = \frac{V(C_f - C_i)}{\text{mmol of reactant}} \times 100, \quad (10)$$

where  $V$  is the cell solution volume (100 ml) and  $C_i$  is determined by solving the following simultaneous equations:

$$E_i = E^\circ + S[-\log C_i] \quad (11)$$

$$E_f = E^\circ + S[-\log C_f]. \quad (12)$$

The initial and final cell potentials,  $E_i$  and  $E_f$ , are determined from the experimental temporal cell potential graph. The initial concentration,  $C_i$ , is known and  $C_f$  and  $E^\circ$ , the constant Nernst equation factor, are the unknowns. Blank experiments (no UV radiation) give constant cell potentials with time. However, the reactant is slowly carried out of the reaction flask. The reaction cannot be performed without nitrogen flow, however, because insufficient pressure is generated to force the HI out of the flask. Thus, the calculated product yields underestimate the bounds on the true product yields.

### 3. Results and discussion

In Fig. 2 are shown a temporal curve with hydronium ion monitoring and a temporal curve with iodide ion monitoring for the 253.7 nm photolysis of iodomethane. The yield results are shown in Table 1. The percentage yields are greater when the condenser is held at the lower temperature. In the last column of Table 1 is shown the ratio of the percentage yield determined by hydronium ion monitoring to that determined by iodide ion monitoring; it is observed to increase by a factor

Table 1  
HI yields for 253.7 nm photolysis of iodomethane

$T_{\text{COND}}$	$\text{N}_2$ flow <sup>a</sup>	Ion monitored	% Yield	Mean	$Y_{\text{H}^+}^b / Y_{\text{I}^-}$
$0^\circ\text{C}$	32	$\text{H}_3\text{O}^+$	$1.9 \times 10^{-3}$	—	2
$0^\circ\text{C}$	32	$\text{I}^-$	$1.0 \times 10^{-3}$	—	
$0^\circ\text{C}$	32	—	—	—	
$-11^\circ\text{C}$	32	$\text{H}_3\text{O}^+$	0.024 0.049 0.074	0.049	8
$-11^\circ\text{C}$	32	$\text{I}^-$	$3.4 \times 10^{-3}$ $8.3 \times 10^{-3}$	$5.8 \times 10^{-3}$	
$-11^\circ\text{C}$	32	—	—	—	8

<sup>a</sup> Bubbles  $\text{min}^{-1}$ .

<sup>b</sup> Ratio of the % yield based on  $\text{H}_3\text{O}^+$  monitoring to the % yield based on  $\text{I}^-$  monitoring.

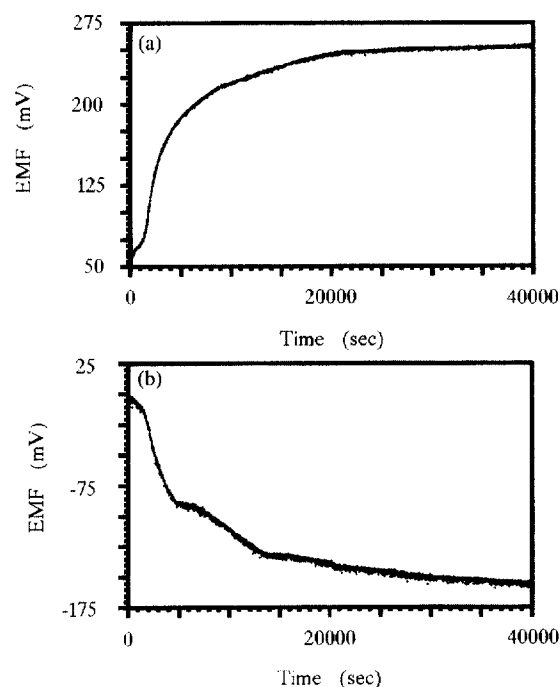


Fig. 3. Temporal  $\text{H}_3\text{O}^+$  curve (a) and temporal  $\text{I}^-$  curve (b) for 2-iodopropane photolysis. Condenser temperature  $-15^\circ\text{C}$  and nitrogen flow 52 bubbles  $\text{min}^{-1}$ .

of four when the condenser temperature is changed from  $0^\circ\text{C}$  to  $-11^\circ\text{C}$ . Since the range for the percentage yields are large, there are two approaches that may be used to obtain an estimate for the lower bound to the actual percentage yield. Statistically, a measure of central tendency of the set of percentage yield values used to calculate the percentage yield ratios, i.e., the set  $\{1.0 \times 10^{-3}, 1.9 \times 10^{-3}, 5.8 \times 10^{-3}, 0.049\}$ , would be used. For sets which have possible outliers, the median is a better measure of central tendency than the mean. The median of the above set is  $3.8 \times 10^{-3}$ . Mathematically, the maximum value of the set would be the best estimate of the greatest lower bound to the actual percentage

Table 2  
HI yields for 253.7 nm photolysis of 2-iodopropane

$T_{\text{COND}}$	$\text{N}_2$ flow <sup>a</sup>	Ion monitored	% Yield	Mean	$Y_{\text{H}}^b Y_{\text{I}}$
0°C	32	$\text{H}_3\text{O}^+$	0.82		
0°C	32	I <sup>-</sup>	0.18		
			0.20	0.19	
0°C	32	—	—	—	4
-15°C	32	$\text{H}_3\text{O}^+$	0.065		
			0.50		
			—	0.28	
-15°C	32	I <sup>-</sup>	0.019	—	
-15°C	32	—	—	—	15
-15°C	52	$\text{H}_3\text{O}^+$	3.68	—	
-15°C	52	I <sup>-</sup>	0.092		
			0.21		
			0.44		
			—	0.25	
-15°C	52	—	—	—	15

<sup>a</sup> Bubbles  $\text{min}^{-1}$ .

<sup>b</sup> Ratio of the % yield based on  $\text{H}_3\text{O}^+$  monitoring to the % yield based on I<sup>-</sup> monitoring.

yield. That value is 0.049. The two estimates differ by a factor of about 13.

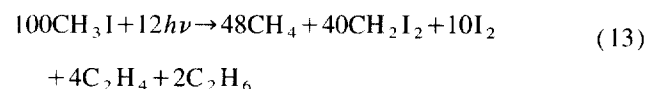
In Fig. 3 are shown a temporal curve with hydronium ion monitoring and a temporal curve with iodide ion monitoring for the 253.7 nm photolysis of 2-iodopropane. The yield results are shown in Table 2. When the temperature is lowered to -15°C with the same flow rate, the percentage yield decreases. However, the ratio of the percentage yields increases by about a factor of 4, as it does for iodomethane when the temperature is decreased. Increasing the flow rate at this lower temperature causes the percentage yield values to increase. However, the ratio of the percentage yields does not change. The likely explanation for these results is that so much iodine is produced in the photolysis of 2-iodopropane that cooling alone has no significant effect. Increasing the flow rate sweeps the products out faster, so the percentage yields increase. The statistical estimate of the actual percentage yield is 0.26, median of the set {0.019, 0.19, 0.25, 0.28, 0.82, 3.68}. The mathematical estimate to the greatest lower bound of the actual percentage yield is 3.68. The later is a factor of 14 larger than the former.

#### 4. Conclusions

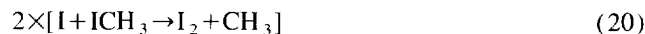
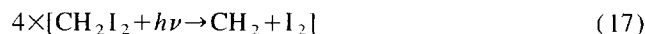
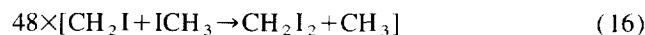
Both iodomethane and 2-iodopropane produce measurable amounts of HI when photolyzed at 253.7 nm. For similar temperatures, the ratio of the yield from hydronium ion monitoring to the yield from iodide monitoring is a factor of two larger for 2-iodopropane than for iodomethane. This is due to the greater amount of iodine carried over into the electrochemical cell when 2-iodopropane is used as the reactant, which causes the equilibrium of Eq. (9) to shift more to the

right for 2-iodopropane than for iodomethane. The fourfold increase in the ratios for each reactant when temperature of the condenser is lowered cannot be explained at this time, because fundamental kinetic data and thermodynamic data for the system are unknown. However, the fact that about a fourfold change is observed for two different reactants, seems to support the conjecture that one or more uncontrolled factors are responsible for the poor precision of the measurements. Further support for this conjecture is the fact that the ratios of the mathematical and statistical estimates to the actual percentage yields for the two reactants are numerically about the same. Greater control could probably be obtained by the use of a more sophisticated generator, but our experiments have been undertaken with the goal of developing a simple, field deployable HI gas generator.

In the case of the photolysis of 2-iodopropane, we have observed that large amounts of iodine in the reaction flask appear to quench HI production. This leads us to investigate the possibility that reduction of iodine in the reaction flask accounts for the increased yields of HI at lower temperature for iodomethane photolysis. We consider the product yields (average of the two experiments reported in Table 2 of Ref. [8]) and determine the best combination of elementary reactions which fit the yield data. The products and their yields in terms of % moles  $\text{CH}_3\text{I}$  are as follows:  $\text{CH}_4$  (52.8%),  $\text{C}_2\text{H}_4$  (5.6%),  $\text{C}_2\text{H}_6$  (5.4%),  $\text{CH}_2\text{I}_2$  (36.0%) and free  $\text{I}_2$  (not specified, because not independent of previous products). Using elementary equations and minimizing the sum of squared errors for the calculated product yields in terms of % moles  $\text{CH}_3\text{I}$ , the best fit is given by the equation



which is the sum of the following elementary equations (weights shown outside of square brackets).



Notice that diiodomethane photolysis accounts for 2/3 of the iodine formed. At the lower temperature, both iodine and diiodomethane are more effectively kept from returning to the reaction flask, and the quenching of HI production is reduced. This is confirmed by visual observation, where patches of violet crystals (iodine) and pale, tannish crystals (diiodomethane) are seen clinging to the inner tube after a run. The pale, tannish crystals melt as the Dewar warms to room temperature. Even though the abundant production of

iodine undoubtedly reduces the potential yield of HI from 2-iodopropane, the yields of HI from the photolysis of 2-iodopropane are still about a factor of 70 higher than those from the photolysis of iodomethane.

In order for a reaction to be useful as a source of calibrant HI, we have estimated that a yield of at least 1% is needed. Using the maximum function estimate, we would conclude that the threshold has been exceeded for 2-iodomethane. However, using the more conservative statistical estimate, we would conclude that the threshold has not been exceeded. Because we cannot consistently get yields greater than 1% with high precision at this time, photolysis of alkyl iodides is not useful for calibrant HI generation.

### Acknowledgements

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Department of the Army position unless so designated by other authorized documents.

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