Photochemical Isotope Separation of Hg-196 by Reaction with Hydrogen Halides

Christopher R. Webster and Richard N. Zare*

Department of Chemistry, Stanford University, Stanford, California 94305 (Received: November 26, 1980; In Final Form: February 11, 1981)

The rarest of the naturally occurring isotopes of mercury, [196]Hg (0.146% abundance), has been photochemically separated by reaction with hydrogen halides as scavengers of the excited Hg($^3P_1$) atoms. A separation of 2–3 mg/h of enriched calomel product is achieved by using a monoisotopic lamp as an excitation source. The product contains 22 ± 8% of the [196]Hg in the feedstock. For the HCl reaction the enrichment factor is 4.2, for HBr 1.4, while for HI no enrichment is found.

Introduction

Mercury occurs naturally as a mixture of seven isotopes of which the lightest, [196]Hg, has an abundance of only 0.146%. The separation of Hg-196 from natural mercury has practical application in the preparation, through nuclear reaction, of radioactive Hg-197, a γ emitter used for cerebral blood-flow measurement and brain-scanning with scintillation detection techniques.[1] To date, the highest enrichments and yields of the isotopes of mercury have resulted from photochemical separation, that is, monoisotopic 6^3P_1–6^1S_0 excitation at 253.7 nm followed by chemical reaction to form a stable, separable product.[2]

On a more fundamental basis, the extent to which mercury compound formation occurs in a primary process can be determined from isotopic analysis of product from the photosensitized reaction. The primary processes in reactions initiated by photoexcited mercury isotopes have been studied in detail by Gunning and co-workers,[3] who investigated enrichment of Hg-198, Hg-201, and Hg-202 from natural mercury using various gaseous substrates. In particular, high product yield and enrichment (≃85%) of these isotopes was obtained by using hydrogen chloride as substrate with added butadiene. The enrichment is defined here as the final isotopic abundance over the initial isotopic abundance. Mercury enriched in Hg-196 has previously been separated by an oxygen/butadiene reaction[4] producing very high enrichment (7500%) but poor product yield (1 mg/day).

We report here photochemical separation of Hg-196 by reaction with hydrogen chloride and hydrogen bromide, patterned after the pioneering work of Gunning and co-workers. The HCl substrate produces both high enrichment (≃320%) and high product yield (2.5 mg/h). Unenriched product was obtained by using hydrogen iodide as substrate. For a hydrogen halide, HX, the isotope specific reaction is

$$^iHg(^3P_1) + HX \rightarrow {}^iHgX + H$$
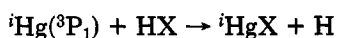
followed by recombination

$$^iHgX + {}^iHgX \xrightarrow{M} {}^iHg_2X_2$$
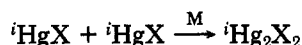
where energy is transferred to the wall or suitable third body, M. The separation is therefore completed by the formation of a solid mercurous compound precipitated from the gas phase.

Separation Apparatus

Figure 1 shows a diagram of the photochemical separation apparatus, and Figure 2 details the reaction cell and the mercury lamp which are at the heart of the experiment. The flow system is constructed mainly in borosilicate glass, with the reaction cell and the inner jackets made from quartz to allow transmission of ultraviolet radiation. Calibrated flowmeters (Matheson) allow controlled amounts of the hydrogen halide (HCl, HBr, or HI) gas to be mixed with a fractional amount of 1,3-butadiene and passed through the reaction cell illuminated by 253.7-nm radiation. All reactant gases used are of the highest purity commercially available (>99.9% for HCl). Before entry into the reaction cell, the butadiene gas passes through a mercury saturator—a temperature-regulated copper block containing a cell of hot liquid mercury over which the gas flows.

The electrodeless "monoisotopic" lamp is a sealed Vycor tube ~10 cm long, containing ~2 mg of mercury enriched in Hg-196 to 35% abundance and 1 torr of neon. The lamp discharge is initiated by a tesla coil and maintained by 2450-MHz radiation from a microwave generator (Scintillonics) using a medical diathermy cone. When the discharge is first struck, orange neon emission dominates until the mercury has warmed sufficiently to carry the discharge, the lamp then taking on its characteristic pale blue color. A flow of dry nitrogen gas cools the lamp to 25–30 °C, the temperature being continuously monitored by a thermometer directly supporting the Vycor lamp.

The quartz cooling tube is surrounded by a cylindrical Teflon tube (see Figure 2) with a vertical slot cut out of it. Rotation about the lamp axis by means of geared motor and drive belt allows the mercury lamp emission to be interrupted at ~3 Hz. This facility was introduced to avoid the unwanted effects of isotope depletion of the active mercury sample, but experiments show that the flow rates achieved in these studies are high enough to make its use advantageous but not essential. A hollow quartz cylindrical jacket ~1 cm thick surrounds the rotating sector. This jacket contains natural mercury at room temperature and a few torr of nitrogen to quench unwanted resonance fluorescence which may otherwise be excited in the jacket by the mercury lamp. The purpose of this jacket is to further improve the monoisotopic nature of the lamp by naturally selective filtration (see Figure 3 for the natural abundances of the mercury isotopes). A 1-cm jacket of mercury vapor near room temperature, for example, will transmit ~90% of the Hg-196 peak emission while reducing the Hg-202 peak transmission by several orders of magnitude.

The outermost cell of this concentric configuration is the reaction cell itself, an all-quartz hollow jacket of cylindrical

(1) "CRC Handbook of Radioactive Nuclides", 1st ed., CRC Press, Cleveland, OH, 1969, pp 383–94.

(2) C. Bradley Moore and V. S. Letokhov, *Chem. Biochem. Appl. Lasers*, **3**, 89 (1977).

(3) H. E. Gunning and O. P. Strausz, *Adv. Photochem.*, **1**, 209 (1963), and references therein.

(4) J. P. Morand, M. Wacongne, and E. Roth, *Én. Nucl.*, **10**, 362 (1968).
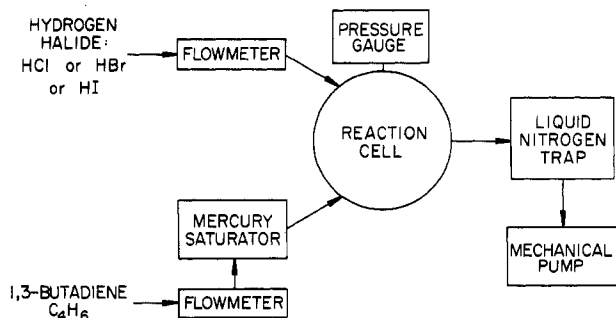
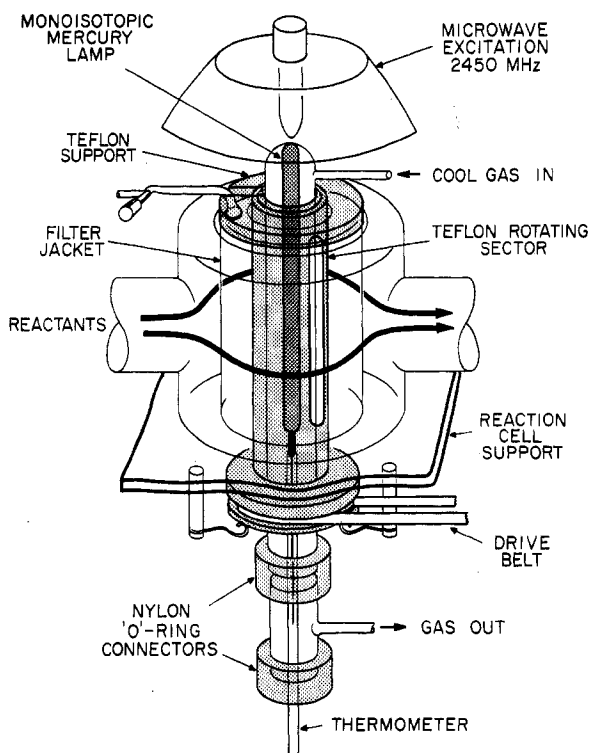**Figure 1.** Schematic of the mercury photochemical separation apparatus.

Figure 2. The monoisotopic lamp and reaction cell.

NATURAL MERCURY ABUNDANCE (%)

196	0.146	201	13.22
198	10.02	202	29.80
199	16.84	204	6.85
200	23.13		

COMPONENTS TO THE 253.7 nm LINE

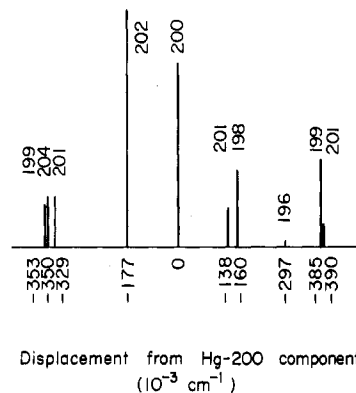Displacement from Hg-200 component
(10^{-3} cm^{-1})

Figure 3. Hyperfine components of the 253.7-nm mercury line. The displacements from the Hg-200 component are converted from F. Bitter, *Appl. Opt.*, 1, 1 (1962). The source of discrepancy between these values and those of ref 2 and 4 is not known.

geometry ~10 cm in diameter, 10 cm high, with an interwall thickness of ~1 cm and an inner volume close to 0.3 L. The inlet and outlet arms to the cell are ~3 cm in diameter, the outlet leading to a large liquid-nitrogen trap backed by a mechanical pump. Since all reactants used are condensibles, pumping is primarily cryogenic.

At the end of a run (4 h, typically) the fine white powder (for HCl and HBr) or yellow powder (for HI) which collected uniformly over the walls of the reaction vessel was removed for analysis. Several attempts were made (with varying degrees of success) to convert the solid product into mercury metal by dissolution in EDTA followed by electrochemical removal of the metal from the solution.[3] Instead, mass-spectrometric analysis was used, employing a direct inlet probe for solid samples. Before product removal, the cell is pumped on for at least 24 h to remove any natural mercury contamination by surface adsorption. The mercurous halides Hg_2Cl_2, Hg_2Br_2, and Hg_2I_2, which lock the reacted mercury into product, sublime at temperatures of ≈450, 390, and 290 °C, respectively. These temperatures are easily reached, and the enriched product is therefore sublimed from the quartz cell onto a collecting plate and the mass spectra of various grains of the solid recorded. For each run reported here, two or three samples were analyzed from the product, and each analysis was

bracketed by natural mercury runs for calibration purposes.

Ability to Separate Hg-196

Separation of the isotopes of mercury by photochemical means using 253.7-nm radiation has been established by several experiments, beginning with that of Zuber[5] in 1935. Successful photochemical separation of a single isotope requires that two fundamental conditions be fulfilled: (i) The spectral bandwidth of the exciting mercury lamp or laser[6] source must be sufficiently narrow to excite only the isotope of interest, the specificity depending on both the spectral bandwidth and the profile of the 253.7-nm line (see Figure 3). (ii) A substrate must be found that reacts with excited mercury atoms to form a stable, separable compound but has no reaction with unexcited atoms. Furthermore, both the substrate and reaction product must be photochemically stable in the presence of 253.7-nm radiation. Condition i is satisfied in the experiments reported here by using a "monoisotopic" mercury lamp and filter combination. Cooling of the lamp below ~35 °C is necessary to avoid problems of self-reversal which otherwise serve to broaden the spectral bandwidth and thereby reduce the isotope specificity. The profile of the 253.7-nm line referred to in condition i includes not only the extent to which any isotopic lines are overlapped within their Doppler widths but also any homogeneous or inhomogeneous broadening resulting from the atomic mercury density and substrate pressure used.

Isotope depletion is an unwanted effect. In a static system, as all of the Hg-196 available is converted into product, the wings of the lamp emission profile take on an increasing importance by eventually separating out the other isotopes, the result producing a less enriched or an unenriched compound. Similarly, in a flow system a precipitate highly enriched in Hg-196 may build up at the reactant entrance to the excitation region, while a pre-

(5) K. Zuber, *Nature (London)*, 136, 796 (1935).
(6) C. R. Webster, L. Wöste, and R. N. Zare, Opt. Commun., 35, 435 (1980).

TABLE I: Experimental Conditions for the HCl Reaction

	run 1	run 2
microwave excitation, W	35 ± 5	18 ± 2 (2450 MHz)
lamp temp, °C	26 ± 2	30 ± 0.5
rotating sector, Hz	3	not used
HCl Flow rate, cm^3 s^{-1}	600 at 5 torr	1500 at 2 torr
C$_4$H$_6$ flow rate, cm^3 s^{-1}	500 at 2 torr	2630 at 0.75 torr
total cell press., torr	7	3
^{n}Hg temp, °C	73	105
estimated cell vol, L	0.3	0.3
estimated passage time through cell, s	0.5	0.1
duration of run, h	4	4
estimated product yield, mg	≤ 2	10 ± 2
(^{196}Hg in product)/ (^{196}Hg passed through cell), %	a	22 ± 8

a Not determined.

TABLE II: Enrichment Factors for Hydrogen Halide Scavengers

	enrichment factor, β^a				
	HCl reaction		HBr reaction		HI reaction
isotope	1	2	1	2	1
196	2.3	4.2	1.4	1.4	1.0
all other isotopes	1.0	1.0	1.0	1.0	1.0

a For definition, see text, eq 1. These values are accurate to ± 0.1.

cipitate depleted in Hg-196 may build up near the exit; collecting both deposits and mixing them then produces a sample of less apparent enrichment. Gunning[7] first recognized this problem and successfully experimented with the use of intermittent illumination by means of a rotating sector constructed to reduce the time of exposure to radiation of a given mercury sample. We follow this example in our experiments.

Hydrogen Chloride Reaction

The hydrogen chloride reaction

$$^{196}\text{Hg}(^3\text{P}_1) + \text{HCl} \rightarrow {}^{196}\text{HgCl} + \text{H}$$
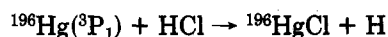
in which the recombination

$$^{196}\text{HgCl} + {}^{196}\text{HgCl} \rightarrow {}^{196}\text{Hg}_2\text{Cl}_2$$

produces mercurous chloride (calomel), fulfills the second condition for separation set out in the previous section. The chloride, precipitated as a fine white powder, is only negligibly decomposed by light and may be sublimed at ~450 °C without melting from the reaction vessel.

The experimental conditions for two 4-h runs using the HCl reaction are given in Table I, and the results concerning the achieved enrichment in Hg-196 are included in Table II. The main differences between runs 1 and 2 are the higher reactant flow rate and the lower cell pressure used in the second experiment. In Table I, the ^{n}Hg temperature refers to the temperature of the liquid mercury in the saturator. The temperature of the mercury vapor in the reaction cell is estimated to be ~30% of this value. In run 2, the absorption by the discharge of the available microwave radiation was improved. This resulted in a more efficient lamp, requiring, therefore, less power from the microwave generator, as indicated in Table I.

(7) H. E. Gunning, *J. Chim. Phys. Phys.-Chim. Biol.* **60**, 197 (1963).

We define the enrichment factor β to be the ratio of the final isotopic ratio to the initial isotopic ratio,[2] i.e.

$$\beta = \frac{[^{196}\text{Hg}]_f / \sum_i [^i\text{Hg}]_f}{[^{196}\text{Hg}]_0 / \sum_i [^i\text{Hg}]_0} \quad (1)$$
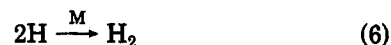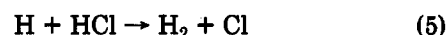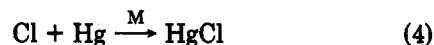
where the summation is over all isotopes.

We find that run 1 produces an enrichment factor for Hg-196 of 2.3 while run 2 produces one of 4.2. This trend, that high reactant flow rates, low reactant pressures, and increased addition of 1,3-butadiene favor the specificity of separation, is in accord with previous observations made when separating other isotopes of mercury by using the HCl reaction.[3]

A reaction scheme must include the following steps:

$$^{196}\text{Hg} + \text{HCl} \rightarrow {}^{196}\text{HgCl} + \text{H} \quad (2)$$

$$^{196}\text{Hg} + \text{HCl} \rightarrow {}^{196}\text{Hg} + \text{Cl} + \text{H} \quad (3)$$

The generation of hydrogen and chlorine atoms is an important isotope scrambling reaction which makes the isotope separation less efficient than suggested by reaction 2 alone. The scrambling occurs through reactions of the type

$$\text{Cl} + \text{Hg} \xrightarrow{\text{M}} \text{HgCl} \quad (4)$$

$$\text{H} + \text{HCl} \rightarrow \text{H}_2 + \text{Cl} \quad (5)$$

$$2\text{H} \xrightarrow{\text{M}} \text{H}_2 \quad (6)$$

Reaction 4 will produce calomel with natural isotopic content. The addition of 1,3-butadiene inhibits unwanted side reactions through polymer formation:

$$\text{C}_4\text{H}_6 + \text{H} \rightarrow (\text{C}_4\text{H}_7) \rightarrow (\text{C}_4\text{H}_7)_n \quad (7)$$
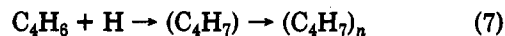
The mole fraction of 1,3-butadiene used compromises between enrichment and yield, since its addition, while substantially increasing the enrichment in Hg-196, reduces the product yield, partly through quenching of the excited $^3\text{P}_1$ mercury atoms. The increased product yield in run 2 given in Table I is not in disagreement with the above statement, since it arises only because of the higher mercury vapor pressure in the cell during reaction. By weighing the liquid mercury in the saturator before and after the experiment, including a small correction for metal condensed to the wall before entry into the reaction cell, and comparing its weight to that of calomel produced by the reaction, we have estimated the ratio of Hg-196 in the product to Hg-196 passed through the cell to be 0.22 ± 0.08.

In the reaction of Hg-196 with hydrogen chloride, the calomel product is synthesized by the recombination

$$^{196}\text{HgCl} + {}^{196}\text{HgCl} \xrightarrow{\text{M}} {}^{196}\text{Hg}_2\text{Cl}_2 \quad (8)$$
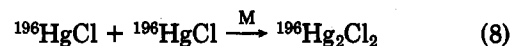
where energy is transferred to the wall or a suitable third body, M. This reaction has a very high rate constant. The rapidity of reaction 4 implies that the side reactions 9 and 10 are negligibly small.

$$\text{HgCl} + \text{Cl} \xrightarrow{\text{M}} \text{HgCl}_2 \quad (9)$$

$$\text{Cl} + \text{Cl} \xrightarrow{\text{M}} \text{Cl}_2 \quad (10)$$

In conclusion, the generation and reactions of the chlorine atom through the isotopic scrambling reaction 4 limit the enrichment process. Furthermore, the H atoms generated in reaction 3 serve to increase the Cl atom concentration through reaction 11, although the addition

$$\text{H} + \text{HCl} \rightarrow \text{H}_2 + \text{Cl} \quad (11)$$
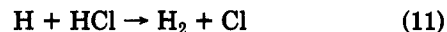
of 1,3-butadiene does inhibit this reaction through polymer formation. The inefficiency of 1,3-butadiene in scavenging Cl atoms in the HCl reaction has been established[8] by its inability to produce an effect on mercury isotope enrichment using other calomel-forming substrates such as the alkyl chlorides.

Calomel is stable in the presence of 253.7-nm radiation and is thought not to undergo, to any appreciable extent, exchange reactions such as

$$^{n}Hg + {}^{196}Hg_2Cl_2 \rightarrow {}^{196}Hg^{n}HgCl_2 + {}^{196}Hg \qquad (12)$$

where n represents mercury with naturally occurring isotopic composition.
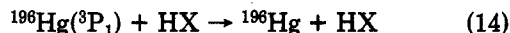
Hydrogen Bromide and Hydrogen Iodide Reactions

Separation of Hg-196 was attempted by using hydrogen bromide and hydrogen iodide as scavengers. Conditions similar to those used in the HCl run 2 were tried, with total reactant pressures in the cell of 2–4 torr. The results of two runs using HBr under identical conditions, and a single run using HI, are given in Table II. Thus, while the HI reaction produces no enrichment, the HBr reaction produces an increase in the Hg-196 abundance according to an enrichment factor of 1.4. The product yield in the HBr reaction was similar to that in the HCl reaction, producing a white powder that turned gray in color on prolonged exposure to light. The HI reaction produced substantially more product, a dirty-yellow colored powder turning slightly green when exposed to light and heated for removal from the cell by sublimation.

The principal reactions of excited Hg-196 with HBr and HI are reactions 13 and 14, where X represents the halogen

$$^{196}Hg(^3P_1) + HX \rightarrow {}^{196}HgX + H \qquad (13)$$
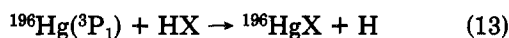
(8) H. E. Gunning, *Can. J. Chem.*, **36**, 89 (1958).

$$^{196}Hg(^3P_1) + HX \rightarrow {}^{196}Hg + HX \qquad (14)$$

atom. However, nothing is known about the branching ratio of reaction 13 to reaction 14. A set of reactions similar to the HCl reactions 4–12 must also be possible for the HBr and HI systems.

The experimental result that mercury can be enriched in Hg-196 by reaction with HBr indicates that reaction 13 is an important primary reaction. Why this reaction produces similar product yield yet lower enrichment than the HCl reaction may be due to an increased importance in exchange reactions like reaction 12 or the scrambling reaction of eq 4. Although Br atoms are less reactive than Cl atoms, their number may be increased by photodissociation of the reactant HBr in the 254-nm spectral region.

The negative result of the HI reaction is not surprising considering that both the reactant HI and the product HgI are photochemically unstable in the 254-nm spectral region. This will increase the nonspecific routes of isotope scrambling leading to unenriched product. Exchange reactions, such as reaction 15, which also lead to isotope

$$^{n}Hg + {}^{196}Hg_2I_2 \rightarrow {}^{196}Hg^{n}HgI_2 + {}^{196}Hg \qquad (15)$$

scrambling are thought likely in view of the instability of Hg_2I_2.

The sources contributing to isotope scrambling in this system continue to be a puzzle. However, this study clearly demonstrates the feasibility of separating Hg-196 by photochemical means using reaction with HCl or HBr. The problems associated with scaling this system to larger throughput are many, but the recent development[6] of a single-mode CW UV laser source ($\leq$0.1-GHz line width) makes possible future studies that will elucidate the practical limits of this isotope separation scheme.

Diatomic Molecule Dissociation. A Vibrating-Rotor Quantum Theory Including Nonequilibrium Effects

William G. Valance

Department of Chemistry, Queens College of The City University of New York, Flushing, New York 11367
(Received: September 29, 1980)

A quantum theory for diatomic molecule dissociation including vibrational nonequilibrium effects is derived here on the basis of the ET (energy transfer) mechanism, and the H_2, N_2, O_2, Cl_2, Br_2, and F_2 dissociation rate constants, k_d, and activation energies, E_a, are calculated and compared to experimental results for temperatures, $T > D_0/(20R)$. The theory assumes (1) rotational equilibrium and (2) a rotating Morse oscillator model for the diatomic molecule with an exponential repulsive interaction between the molecule and its colliding partner. The vibrational energy transfer rates were obtained from a modified SSH theory, while the collisional dissociation rates for a molecule in a specific vibrational level, $k_d(n)$, are found by using a DWB approximation and a semiclassical approach. A novel algorithm for obtaining the nonequilibrium distribution is presented. The activation energy, E_a, is approximately $D_0 - RT/2 - h\nu/(e^{h\nu/(kT)} - 1)$. Agreement with experimental results is within experimental error except for F_2, which has an exceptionally strong F–Ar interaction. The correct rotational statistics and nonzero $k_d(n)$ for levels below the top vibrational level must be included in the theory to obtain agreement between theoretical and experimental k_d values.

Introduction

Many theories for diatomic molecule dissociation include nonequilibrium effects due to depletion of the upper vibrational energy levels by reaction.[1-7] Some of these theories[1,3] have ignored the effect of molecular rotations and assumed also that the collision-induced dissociation

(1) H. S. Johnston and J. Birks, *Acc. Chem. Res.*, **5**, 327 (1972).