Isotopically Selective Photochemistry of Bromine*

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A tunable narrow-frequency laser is used to produce an isotopically selected reaction product of bromine. Natural Br_2 ($^{79}Br/^{81}Br = 1$) is photopredissociated by selective excitation into the $^3\Pi_{0^+u}$ state. Bromine atoms enriched in one isotope react with HI before scrambling occurs to produce 80–85% $H^{81}Br$. The method should yield an efficient technique for isotope separation. Spectroscopic requirements and the optimum reaction conditions are discussed. The relative amount of nonselective product from excitation of the Br_2 continuum is determined.

The development of tunable lasers has stimulated a resurgence of interest in selective photochemical reactions for isotope separation. Recent papers review the requirements and suggested methods for laser isotope separation.[1,2] We describe here an isotopically selective photochemical reaction sequence for bromine (natural abundance 50.5% ^{79}Br, 49.5% ^{81}Br). Although a number of recent reports of laser isotope separation require two-step photoionization or dissociation,[3-5] here we use a single photon absorption followed by molecular predissociation.[6] Tuning of the laser to desired isotopic absorption lines is facilitated by visual observation of fluorescence in cells containing $^{79}Br_2$, $^{81}Br_2$, and natural $^nBr_2$. We choose here to detect the product isotopic enrichment from the vibrational chemiluminescence of the $H^{79}Br$ and $H^{81}Br$ produced in the reaction $Br + HI \rightarrow HBr(v = 0, 1, 2) + I$.[7] The advantage of this technique over the usual mass spectral determinations is that the isotopically selective photochemical steps are confirmed independently of subsequent slower chemistry. Practical separation devices may then be devised with better success.

The 558- and 532-nm lines of a Chromatix frequency-doubled neodymium-doped yttrium-aluminum-garnet (YAlG) laser (1 mJ, 10^{-7}-sec pulses, 80 pulses/sec) are used for excitation of Br_2. The ~1-cm^{-1} gain bandwidth of the YAlG laser is narrowed by an internal etalon with a finesse of 7. The resulting spectral output is 1.2 GHz wide as observed with a spectrum analyzer, and is smoothly tunable over the YAlG gain by angular adjustment. A 50-mm-diam quartz cell is used for the reaction studies. The HI flows into the cell from 25-mm tubing. The Br_2 is injected into the HI stream by a series of five 0.4-mm pinholes at the cell entrance. The Br_2 jets point in the direction of the flow. 50 cm of 14-mm-diam tubing connect the cell to liquid-nitrogen traps for pumping. An all-Monel MKS Baratron capacitance manometer is used to measure the pressures of HI and Br_2. Br_2, the minor constituent, is added after the HI flow is established.

Infrared fluorescence is observed with a Ge:Cu photoconductive detector (~15°K). The detector, cell, lens geometry, and signal averaging system have been described previously.[8] A narrow-band filter transmits primarily the HBr $1 \rightarrow 0$ R branch. About 30% of the total signal is from the shorter-radiative-lifetime $2 \rightarrow 1$ fluorescence produced in the Br + HI reaction. Quartz filter cells of $H^{79}Br$ and $H^{81}Br$ containing 30 Torr in a 5-cm path length completely block the $H^{79}Br(v = 1)$ and $H^{81}Br(v = 1)$ emissions, respectively. In a separate experiment the ratio of transmissions of the desired $HBr(v = 1)$ isotope signals was accurately measured. Isotopic gases are prepared from $Na^{79}Br$ (99.75%) and $Na^{81}Br$ (97.8%) obtained from Oak Ridge National Laboratory.

The primary photochemical step is excitation of Br_2 into the bound levels of the $^3\Pi_{0^+u}$ state (Fig. 1) followed by predissociation and collision-induced dissociation. It has been proposed that this type of excitation could lead to isotopically selective chemistry.[9] The laser is tuned to absorption lines by visual observation of fluorescence from cells each containing 1 Torr of $^{79}Br_2$, $^{81}Br_2$, and $^nBr_2$. With experience, reasonable estimates of the relative magnitudes of absorption lines can be made. The strongest lines are easily picked out. Lines can be observed which appear to discriminate in favor of $^{81}Br_2$ over $^{79}Br_2$ (and vice versa) by as much as 2 orders of magnitude. Continuum absorption exists throughout the 558- and 532-nm regions. The laser can be tuned to wavelengths for which no line fluorescence is observed and only the nonselective continuum absorbs.

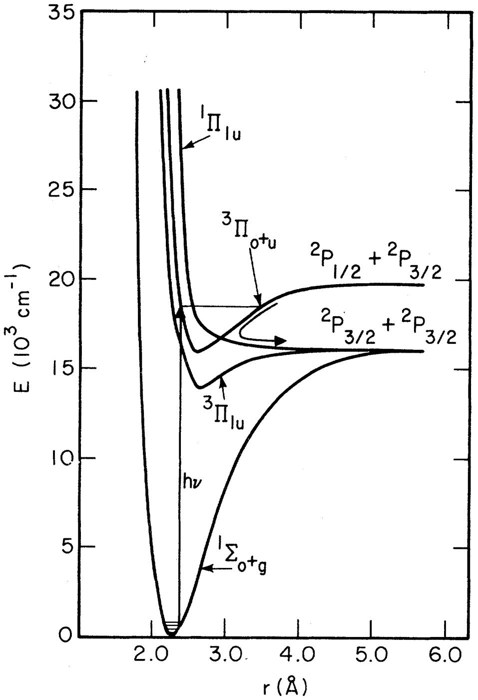

FIG. 1. Approximate potential diagram for Br_2 [D. B. Gibbs and E. A. Ogryzlo, Can. J. Chem. 43, 1905 (1965)] showing excitation step and collisionally induced dissociation at 558 nm.

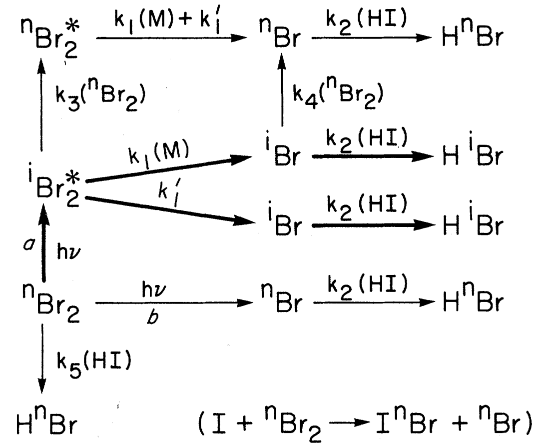

FIG. 2. Isotopically selective reaction sequence for bromine. Here, *a* is the line absorption and *b* is the continuum absorption; *n* denotes nonselected and *i* isotopically selected bromine. k_1 is the rate constant for collisionally induced dissociation and k_1' the predissociation rate. k_2 is the rate constant for the reaction Br + HI, k_3 for electronic energy transfer, k_4 for Br atom exchange, and k_5 for the bimolecular reaction Br_2 + HI. The heavy arrows are the desired separation path. *M* is either Br_2 or HI.

The relative absorptions of lines versus continuum were measured at 558 and 532 nm. The product-HBr vibrational emission intensity is observed as the laser is tuned on and off the fluorescence line. The strongest line of a single isotope at 532 nm has a line-to-continuum ratio (a:b) of 1:4. At 558 nm, however, several lines of single isotopes have line-to-continuum ratios of 3:2. This is not unexpected, since the continuum absorption is rapidly decreasing toward longer wavelengths.[10] At room temperature the Doppler width of Br_2 is 500 MHz, much less than our 1.2-GHz laser. A laser with a 200-MHz linewidth at 558 nm could provide a line-to-continuum ratio a:b of greater than 4:1, or an abundance of the selected isotope in the excitation step of $(2a+b)/2(a+b)=90\%$. With our laser the maximum abundance is presently limited to about 80%. It may be possible to increase the ratio a:b by tuning to longer wavelengths where the continuum approaches zero or by exciting just below the dissociation threshold. However, the line absorptions would be weaker. The ratio a:b may also vary with temperature.

Predissociation, k_1', and collisionally induced dissociation, $k_1(M)$, in Fig. 2 are discussed in more detail in a recent review.[11] With 558 nm, predominantly ground-state Br atoms are produced. At 532 nm, a large fraction of electronically excited atoms is detected by electronic-to-vibrational transfer processes.[12] The only lifetime and quenching studies[13] on Br_2 to determine k_1 and k_1' are in doubt.[10] However, if Br_2 is similar to I_2, the collisionally induced dissociation cross sections may be gas kinetic. The first attempt to separate the isotopes of Br_2 used a ruby laser to excite the $^3\Pi_{1u}$ state.[14] The rapid collisional dissociation produced atoms which on collision with $^nBr_2$ became isotopically scrambled.

A rapid chemical scavenging method is necessary to trap the isotopically selected atoms. The choice of HI (Fig. 2) is a favorable one. An estimate of the rate constant k_2 measured in our system with the infrared fluorescence method[7] is $(1.1\pm0.4)\times10^{-11}$ cm^3/molecule sec. Rate measurements for Br + HI and Br* + HI are in progress.[15]

In order for the desired reaction sequence to reflect the selectivity of the excitation step, the scrambling processes k_3, k_4, and k_5 must be suppressed. The necessary conditions are that $k_1(M)+k_1'\gg k_3(Br_2)$, that $k_2(HI)\gg k_4(Br_2)$, and that the

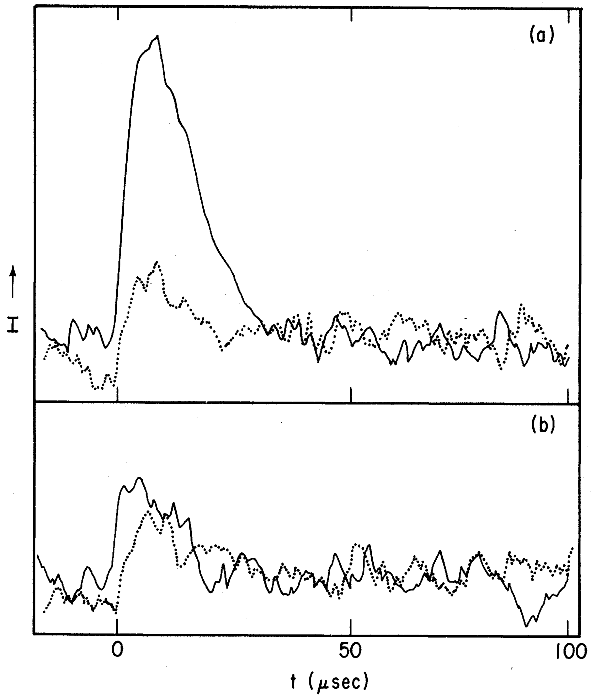

FIG. 3. (a) $H^{81}Br$ ($v = 1$) emission intensity plus 2→1 leakage. (b) $H^{79}Br$ ($v = 1$) intensity plus 2→1 leakage. The solid curves are with excitation of $^{81}Br_2$ at 558 nm. The dotted curves are for excitation of the continuum only. The rise time after the laser pulse is the reaction rate k_2 and the decay is $V \rightarrow V$ of HBr ($v = 1$) to HI ($v = 1$) [H.-L. Chen, J. Chem. Phys. 55, 5557 (1971)].

time in the flow is much shorter than the prereaction rate $k_5(Br_2)(HI)$. Some enrichment is observed with flow ratios $HI:Br_2$ of 20:1, although the best obtained was with 50:1. Thus, the first two of these conditions may be fulfilled. If the collisionally induced dissociation is quite fast, then the electronic energy transfer k_3 is a minor source of scrambling. The atom exchange k_4 ($^iBr + Br_2 \rightarrow {}^iBrBr + Br$) is the major cause of scrambling the isotopically selected atoms.

Figure 3 shows a typical set of $H^{79}Br(v = 1)$ and $H^{81}Br(v = 1)$ intensities demonstrating the isotopic selectivity of the product HBr after excitation of $^{81}Br_2$ with the 558-nm line. From the previously measured line-to-continuum ratio of 3:2, the maximum product abundance is 80% $H^{81}Br$ and 20% $H^{79}Br$. From the observed signals an estimate of the vibrationally excited product isotope distribution may be calculated. All filter transmission factors (interference and gaseous) are included in the calculation, as well as the leakage of 2→1 fluorescence and the different radiative lifetimes of the 2→1 and 1→0 emissions. The product vibrational distribution is taken to be $(v = 2)/(v = 1) = 1.0$.[16] The product abundance for the ~50:1 flow ratio is 80–85% $H^{81}Br$.

Prereaction, k_5, is a severe practical problem for an isotope separation system. To minimize prereaction, these measurements were carried out in a darkened room with flow rates which exchanged the gases in the cell every 10 msec. These fluorescence results are relatively insensitive to prereaction. However, if as much as 10% prereaction occurs in this experiment, the $H^{79}Br$ and $H^{81}Br$ signals would approach each other by $V \rightarrow V$ transfer[8] before the decays are over. A second chemical problem for practical isotope separation with this sequence is the subsequent reaction of I with Br_2. Iodine atoms react with $^nBr_2$ to produce $IBr + {}^nBr$ with a rate constant of 8.8×10^{-14} cm^3/molecule sec.[17] A regenerative chain scrambling may occur which cannot be prevented by the iodine recombination rate at the low I-atom pressures produced. These difficulties necessitate rapid removal of either the Br_2 or I atoms (or both) at the walls of the reaction chamber.

We have obtained conclusive evidence for an isotopically selective photochemical process in bromine. The single-visible-photon excitation and high enrichment possible make the process attractive for practical isotope separation. The visible and infrared observation techniques used here have wide applicability to other isotopically selective systems. These types of experiment will allow the resolution and assignment of overlapping discrete and continuous spectra, the study of predissociation rates and mechanisms, the measurement of rates of electronic energy transfer, atom exchange, and chemical reaction, and the observation of product energy-state distributions.

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