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DOE/ER/71013--T1

INTERIM REPORT ON MODELING STUDIES OF
TWO-PHOTON ISOTOPE SEPARATION

DOE/ER/71013--T1

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28 January 1975

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ABSTRACT

The two-photon or two-step dissociation method of laser induced isotope enrichment is being modeled for the HBr-NO photochemical system. In the model, H^{79}Br is selectively excited by resonance IR laser radiation and then dissociated by UV radiation. Selectively dissociated Br atoms are scavenged to form isotopically enriched BrNO and Br_2 . This model includes all kinetic and absorption processes found to be significant and the time-varying concentrations of any species involved in a significant process. Among these processes are vibrational energy transfer reactions (including isotopic exchange) involving HBr $v=0-3$, rotational and translational (velocity) relaxation processes, dissociation of HBr in the $v=0-3$ levels, and secondary chemical reactions of the dissociation products.

The absorption and kinetic processes that are most important to ^{79}Br enrichment have been identified and the study of the effects on enrichment upon variation of external parameters (such as reactant pressure, IR or UV source intensity, and temperature) is in progress. Some preliminary results are: (1) intensity of the IR source is usually more important than the UV intensity, (2) chemical reactions are the dominant kinetic processes at lower pressures while energy transfer reactions dominate at higher pressures, (3) kinetic processes usually have greater effect on the isotopic abundance in the products while absorption processes generally have greater effect on the absolute amount of enriched products, (4) isotopic abundance of ^{79}Br in the products can range from 0.55 to 0.80 for the conditions used in the model.

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I. INTRODUCTION

A. Two-photon Isotope Enrichment Method

The two-photon or two-step isotope enrichment method is one of the most promising general methods of laser photochemical isotope enrichment. The first absorption step is the isotopically specific promotion of a ground state molecule to a bound excited state by laser radiation. The second absorption step promotes the excited molecule into a predissociative, dissociative, or ionic state. In this study the method being modeled involves promotion of a molecule to an excited vibrational level using a pulsed IR laser followed by dissociation using a pulsed UV source. A general photochemical enrichment method such as this should be applicable to all molecules.

This two photon method may be divided into four stages: isotopically selective absorption of the first photon from an IR laser, energy transfer processes involving vibrationally excited molecules, absorption of the second photon from a UV source (dissociation), and chemical reactions of the dissociation products to form stable products. Each stage is actually coupled to all other stages since processes classed in different stages simultaneously involve the same species. Thus an accurate model of this method must include (1) all significant kinetic and absorption processes, (2) the concentration of any species involved in these processes and (3) the variation of these concentrations as a function of time.

B. Photochemical systems

Two photochemical systems, involving excitation of a diatomic molecule and of a polyatomic molecule are being modeled. Parametric studies are being performed first on a simple diatomic system where absorption and kinetic processes are better known. The parametric studies will then be extended to model a polyatomic system where less is known about the absorption and kinetic processes. The polyatomic system features the additional complexities of more energy transfer processes, overlapping isotopic spectra and greater energy level density. The model of the

diatomic system will be more accurate while the polyatomic model will be more general.

The diatomic system chosen is the two-photon selective dissociation of HBr followed by radical scavenging of Br and H by NO. The isotopic spectra of HBr in the IR have been resolved and the ground state UV absorption spectrum is well known. The energy transfer processes of hydrogen halides are among the most thoroughly studied and the reactions of NO with H and halogen atoms have been extensively studied. Furthermore, this could be a practical experimental system since the HBr laser is a powerful IR resonance source and the HBr UV absorption spectrum occurs at low enough frequencies to allow strong absorption of UV radiation from either a laser or a conventional wide-band source.

C. Enrichment Criteria

The extent of isotopic enrichment produced by this two-photon method can be measured in several ways. Two measures used in this study are the enrichment ratio and the absolute enrichment. In the HBr system where ^{79}Br is being enriched and the natural abundance of ^{79}Br is taken to be 0.50, the enrichment ratio, α , is defined as

$$\alpha = \frac{2 \times (\text{number of } ^{79}\text{Br atoms contained in products})}{(\text{number of total Br atoms contained in products})} - 1$$

This gives a normalized measure of the increase in isotopic abundance of ^{79}Br . The absolute enrichment β , is defined as the difference between the number of ^{79}Br atoms and the number of ^{81}Br atoms contained in the products.

D. Goals of Modeling Study

The main goals in this study are (1) construction of an accurate and consistent model of the two-photon laser isotope enrichment scheme that includes all significant processes, (2) identification of the important processes and their effects on the extent of enrichment, (3) identification of the important parameters and observation of the dependence of α and β upon parameterization, (4) determination of the range of conditions for which significant enrichment can be obtained, and (5) optimization of the enrichment based on a single combined measure of enrichment.

E. Present Status

The model for the diatomic HBr-NO photochemical system, which includes all processes determined to be significant, has been constructed. The full model contains 25 chemical species, the time dependence of their concentrations, 183 kinetic processes, and 13 absorption processes (under some ranges of initial conditions a simpler model can be used). Some of the processes found to be significant are energy transfer reactions involving vibrationally excited HBr up to the $V=3$ level, dissociation from the $V=0$ and 2 levels of HBr, rotational relaxation processes, translational (velocity) relaxation processes (hole-burning effects), and secondary chemical reactions of the dissociation products. A detailed description of the model is given in Section II.

For the diatomic system, the important processes and their effects on α and β have been identified. In general the absorption processes have a greater effect on β , while the kinetic processes have a greater effect on α . At low pressures chemical reactions dominate kinetic processes while energy transfer reactions dominate at high pressures. The results are given in Section III.

The study of effects on α and β upon variation of external parameters is in progress. The intensity of the IR and UV sources, the frequency of the UV source, and initial pressures have pronounced effects on enrichment. For typical conditions two interesting results are: 1) the intensity of the IR source is more important than the UV intensity and 2) enrichment appears to be a larger function of the energy transfer processes than of the chemical processes.

Under the unoptimized conditions that have been modeled, the range of α has been 0.1 to 0.6 (equivalent to an isotopic abundance for ^{79}Br in the products of 0.55-0.80) and the range of β has been about 10^{12} - 10^{13} molecules/cc (or about 10^{-5} of the initial HBr concentration). Details of the preliminary results are given in Section IV.

Other external parameters that will be investigated are temperature, IR laser linewidth, excitation pulse widths (including a simulation of cw sources), and the delay between the IR and UV pulses. The effect of exciting

an IR overtone transition and the effect of using a broadband UV source will be studied. These studies should yield the range of conditions for which enrichment is possible and the optimization of those conditions.

The studies will be extended to the polyatomic molecule CH_3Br . This system has the additional complexities of relaxation between vibrational modes, possibility of overlapping isotopic IR spectra, and greater energy level density. Emphasis will be placed on the variation of rate constants and extinction coefficients and analysis of the effects of this variation on the important processes.

II. CONSTRUCTION OF MODEL AND IDENTIFICATION OF SIGNIFICANT PROCESSES

A. General Description

The physical system being modeled is a static, homogeneous gas mixture contained in a cylindrical cell. Radiation from the IR and UV excitation sources enter both ends of the cell (to minimize non-uniformity of absorption), interacts with molecules in the complete cell volume, and initiates the enrichment processes. All processes occur uniformly in the cell and interactions with the cell walls are not modeled.

The model includes as variables any chemical species involved in a significant kinetic or absorption process, radiation intensities associated with each absorption process, and the temperature of the system. The variables are interrelated via kinetic or absorption processes where the magnitudes of the interrelations are given by rate constants, extinction coefficients, enthalpy changes, and heat capacities. After the variables, which are functions of frequency and time, are integrated over the (usually small) frequency range where absorption occurs, the system is described by a set of coupled differential equations, where each equation is the time derivative of a variable. The numerical solution of the equations yields the value of each variable from which the value of enrichment criteria such as enrichment ratio, α , or absolute enrichment, β , are computed.

The construction of the HBr - NO diatomic model will be described in four stages: the first absorption step, energy transfer processes (which include rotational-translational as well as vibrational relaxation processes), the second absorption step, and chemical reactions. In each stage the significant processes are identified and the evaluation of the rate constants and extinction coefficients are described. The enthalpy changes, heat capacities, and other thermodynamic values were taken from the JANAF Thermochemical Tables (Ref. 1).

B. The First Absorption Step

The isotopic lines in the fundamental IR absorption spectra of HBr are completely resolved. Since the IR excitation source in this model is a single-line, isotopic HBr laser operating on the $P_1(5)$ transition of $H^{79}Br$, evaluation of the extinction coefficient for just that transition is sufficient. Since the laser linewidth would probably be much smaller than the Doppler width of the absorption line (for an HF laser the laser linewidth is less than 1/100 of the Doppler width) (Ref. 2), the extinction coefficient can thus be taken as the peak extinction coefficient of the Voigt absorption profile (combined Doppler and Lorentzian profile).

The experimental line strengths of Gustafson and Rao (Ref. 3) and either calculated or estimated Lorentzian line broadening parameters were used to calculate the extinction coefficients. During the IR laser pulse (a Gaussian with a 1 μ sec full width at half intensity truncated 1.5 μ sec from the peak) only line broadening from HBr - HBr and HBr - NO collisions need to be considered. The HBr - HBr line-broadening parameter used was that calculated by Benedict and Herman (Ref. 4) while the HBr - NO parameter was estimated to be similar to the experimentally determined HBr - M parameters of Rank and coworkers (Ref. 5). The typical 1.5 mjoule pulse is consistent with the $P_1(5)$ energy that Burak and coworkers (Ref. 6) observed in their multiline HBr laser.

C. Energy transfer Processes: Vibrational Relaxation

Since absorption of the first photon produces a non-equilibrium distribution in the $H^{79}Br$ vibrational levels, the population of these levels will be affected by V-V and V-R, T energy transfer processes. Only HBr V-V energy exchange with HBr and NO need to be considered since concentrations of all other molecules are insignificant during the absorption processes. The HBr - HBr processes either exchange isotopic excitation (eq. 1), or redistribute vibrational energy within an isotopic vibrational manifold (eq. 2 and 3).

In general the HBr - NO processes (eq. 4) lead to a decrease in selective excitation of H^{79}Br .

Tests have determined that only the $v=0-3$ levels of HBr and the $v=0, 1$ levels of NO need to be considered in this model. In a test model that included the HBr $v=4$ levels, the rate of dissociation from the $v=3$ level was less than $1/100$ of the rate of the $v=1$ level at all times. Thus the $v=2$ levels were the highest ones with significant population; since only $\Delta v=\pm 1$ relaxation processes are considered, only the $v=0-3$ levels are necessary in this model. A test model that included the $v=2$ level of NO showed that $\text{NO}(v=1) < 1/100 \text{ NO}(v=0)$ at all times; thus only the $v=0$ and 1 levels are necessary in this model.

For V-V exchange, reactions between a hydrogen halide and a series of collision partners, plots of $P/(\mu_1\mu_2)^2$ vs ΔE are linear when the different collision partners are similar to each other (Ref. 7). P is the probability per collision of energy transfer, μ_1 and μ_2 are the dipole moments of the hydrogen halide and a particular collision partner, and ΔE is the vibrational energy defect of the transfer process. A plot for HBr-HX reactions was made from experimental data (Ref. 8) for HBr ($v=1$) and $\text{HX}=\text{DBr}$, HI , and $\text{HBr}(v=1)$; except for the process $2\text{HBr}(v=1) \rightleftharpoons \text{HBr}(v=2) + \text{HBr}(v=0)$ where experimental data (Ref. 8a, b) were used, the rate constants for all HBr - HBr V-V processes were estimated from the plot. The rate constants for HBr - NO V-V processes were estimated from a similar plot for NO + HX V-V processes where the experimental rates (Ref. 9) were for $\text{HX} = \text{HF}$, DF , HCl , and DCl .

V-T energy transfer processes of $\text{HBr}(v=0-3) + \text{M}$ and $\text{NO}(v=0, 1) + \text{M}$ are included in this model for $\text{M}=\text{HBr}$ or NO . The rate constants for $\text{HBr}(v=i) + \text{HBr} \rightleftharpoons \text{HBr}(v=i-1) + \text{HBr}$ were set equal to the experimentally determined rate (Ref. 10) for $\text{HBr}(v=1) + \text{HBr}(0) \rightleftharpoons 2\text{HBr}(0)$. The $\text{NO}(v=1)$

+ NO $\rightleftharpoons$ NO($v=0$) + NO rate constant was measured by J. C. Stephenson (Ref. 11). The rate constants for HBr(1) + NO $\rightleftharpoons$ HBr(0) + NO and NO($v=1$) + HBr $\rightleftharpoons$ NO($v=0$) + HBr were estimated to be 1/10 of the self relaxation rate of NO. Since the uncertainty in the estimates was large, several rate constants bracketing the estimated value were also used in the model.

D. Energy Transfer Processes: Rotational-translational Relaxation

The absorption of single-line IR radiation also results in a non-equilibrium rotational distribution of both the ground and excited vibrational levels of H⁷⁹ Br. The intensity of the absorption and the rates of the rotational relaxation processes will determine whether the equilibrium distribution is strongly perturbed. A strong perturbation of the $v=0$ distribution, or a strong perturbation of the $v=1$ distributions coupled with saturation effects (when net absorption is reduced significantly by stimulated emission) can reduce the IR absorption relative to the equilibrium case. In the non-equilibrium case only a fraction of the molecules in a vibrational level will be capable of interacting with the IR radiation.

For an inhomogeneously broadened line the IR radiation may also result in a non-equilibrium translational (velocity) distribution in the $v=0$ and $v=1$ levels of H⁷⁹ Br. At low pressures the absorption line is inhomogeneously broadened and the IR radiation can interact only with molecules that have certain velocity components. If the magnitude of absorption per unit time is great enough, the translational or velocity relaxation processes cannot maintain an equilibrium velocity distribution and "hole burning" of the absorption line will occur.

In order to test the effects of rotational and translational relaxation, the IR absorption in a non-equilibrium case with coupled rotational-translational relaxation* was compared with absorption in an equilibrium case. In the equilibrium case the only species were H⁷⁹ Br ($v=0$) and

*Both a rotational relaxation model with translational equilibrium and a translational relaxation model with rotational equilibrium were found to be inadequate. Both models underestimated the total effect of rotational-translational disequilibrium.

H^{79}Br ($v=1$) and the only process was the IR absorption step.

In the non-equilibrium case (see fig. 1A) each of the two vibrational levels is divided into four states $G_R G_T^v$, $B_R G_T^v$, $G_R B_T^v$, and $B_R B_T^v$ where $v=0, 1$. G_R represents states whose molecules have the proper J quantum number for interaction with the radiation ($J=5$ for $v=0$ and $J=4$ for $v=1$) while the B_R states contain molecules with the other J values. G_T represents states in which molecules have the proper velocity component for interaction while B_T represents states in which molecules do not. Thus only molecules in the $G_R G_T^v$ state can interact directly with the IR radiation. Reactions 3, 3', 4 and 4' (see fig. 1A) are strictly translational relaxation processes which do not involve a change in the rotational quantum number. Reactions 5, 5', 6, and 6' are strictly rotational relaxation processes. Reactions 7, 7', 8, and 8' are rotational relaxation processes that also involve a change in translational state. The relative rate constants of reactions 7, 7', 8, and 8' to reactions 5, 5', 6, and 6' depend on the extent of the coupling of translational and rotational relaxation processes.

A special case occurs when the coupling is complete and the relative rate constants for the eight processes are such that the equilibrium between the $B_R G_T^v$ and $B_R B_T^v$ states is maintained. In that case the $B_R G_T^v$ and $B_R B_T^v$ states can be combined into the B_R^v state (see fig. 1B) and the eight processes can be reduced to just four rotational-translational relaxation processes 9, 9', 10, and 10'. The rotational-translational coupling can be considered complete whenever the translational energy (velocity) change upon any rotational relaxation collision is sufficiently large for the molecule to change translational state as well. Then the probability of a change in translational state would only depend on the equilibrium populations of XG_T^v and XB_T^v where $X=G_R$ or B_R . Whenever the translational energy difference associated with the laser linewidth is comparable to or less than the minimum energy defect of a rotational relaxation reaction, rotational-translational coupling is considered complete and $v=0$ and $v=1$ levels of H^{79}Br will be divided into three states as shown in fig. 1B.

1A: Coupled rotational and translational relaxation case

1B: Rotational and translational relaxation case, complete coupling

Figure 1: Rotational and Translational Relaxation Models

For identical initial conditions and rate parameters, absorption in the rotational-translational relaxation case was significantly less than the absorption in the equilibrium case for low initial pressures of reactants. The size of the absorption difference in the two cases was a strong function of the laser line width and rotational relaxation rate; however the experimental values for these two variables have not been measured. Typical values that were used are a laser linewidth less than 1/10 of the Doppler absorption width and a gas kinetic rotational relaxation rate. The coupled relaxation case was used whenever the absorption difference between the two cases was greater than 10 percent. As a rough rule this occurred whenever the Doppler width was comparable to or greater than the Lorentz width due to line broadening.

E. The Second Absorption Step

Since the UV source in the second absorption step couples bound HBr vibrational states to an unbound dissociative state with a steep potential, dissociation can occur from all reasonably populated vibrational levels, even with a single frequency UV source. Thus extinction coefficients for dissociation from the $v=0-3$ vibrational levels of HBr are all needed. The coefficients for the $v=0$ level have been measured by Goodeve and Taylor (Ref. 12). The ratios of the Frank-Condon factor of a given excited vibrational state to that of the ground state were calculated and the results were used to evaluate extinction coefficients of the excited states. In those calculations the harmonic oscillator approximation was used for wave functions of the bound states while the delta function approximation, a reasonable approximation based on other diatomic cases (Ref. 13), was used for the dissociative state. For a particular transition the interatomic distance associated with a particular frequency was estimated from the potential curves of Goodeve and Taylor (Ref. 12). Extinction coefficients at 265nm, 250nm, and 235nm were calculated for the $v=1-3$ states; no distinctions were made for isotopic or rotational-translational states.

The typical UV source used in the model was a single line, 90 mjoule

laser at 265nm. The temporal and spatial profiles of this laser pulse are identical to the IR laser pulse. The energy from this source is comparable to that expected from a commercial visible dye laser and a frequency doubling system with 5 percent conversion efficiency.

F. Chemistry

The original list of chemical reactions considered for modeling included all possible two-body and three-body reactions that had a free energy change of less than +10 kcal/mole and had as reactants HBr, NO, H, Br, or any primary or secondary product of another reaction. Next, bimolecular reactions requiring four-center transition states were eliminated (eg. $\text{Br}_2 + \text{H}_2 \rightleftharpoons 2\text{HBr}$) since these reactions have notoriously high activation energies. Finally, reactions whose elimination as a group from the model did not change the concentration of any bromine containing species by more than 0.2 percent were dropped from the reaction list. The reactions remaining in the model are given in Table 1. All back reactions are included but the kinetic isotope effect, which should be small, is excluded. The variation in rate constant with the vibrational level of a molecular reactant is not included.

The measured rate constants for reactions 7, 12, and 14 (Ref. 14) are used in the model. The rate parameters for reaction 6 have been measured (Ref. 15) for $\text{M}=\text{NO}$ and H_2 ; rates for all other M's were set equal to the rate for $\text{M}=\text{NO}$ since little variation of the rate constant with M has been observed. For reaction 9 rate constants have been established for the 3rd bodies H_2 , Br_2 , HBr, and Br (Ref. 16). Rate constants for HNO and BrNO as the third body were set equal to that of HBr while rate parameters for H and NO were equated with those for Br.

The rate constants for reaction 5 for all M's were set equal to the average of the rate constants experimentally determined for $\text{NO}+\text{F}+\text{NO} \rightleftharpoons \text{FNO}+\text{NO}$ (Ref. 17) and $\text{NO}+\text{Cl}+\text{NO} \rightleftharpoons \text{ClNO}+\text{NO}$ (Ref. 18). Little dependence on M was found for either the fluorine or chlorine reactions. The rate parameters of reaction 10 for all M were equated with the average parameters for $\text{H}+\text{F}+\text{M} \rightleftharpoons \text{HF}+\text{M}$ (Ref. 19) and $\text{H}+\text{Cl}+\text{M} \rightleftharpoons \text{HCl}+\text{M}$ (Ref. 20) for the same reasons.

Reaction

TABLE 1: CHEMICAL REACTIONS

The rate parameters for reactions 11 and 13 were set equal (except for differences in collision frequency) to the experimental parameters of the reaction $\text{H} + \text{HNO} \rightleftharpoons \text{H}_2 + \text{NO}$ (Ref. 14a). The parameters for reaction 8 were equated (again except for a collision frequency correction) with those of the process $\text{Cl} + \text{ClNO} \rightleftharpoons \text{Cl}_2 + \text{NO}$ (Ref. 21).

The activation energies for reactions 16 and 17 were equated with the experimentally determined energy of reaction 18. (Ref. 22).

Both reactions 16 and 17 were assigned gas kinetic pre-exponential rates to prevent underestimation of the isotope exchange reaction. The activation energy for reaction 15 was estimated to be 2 kcal/mole less than that of reaction 16 since the activation energies for reactions 19 and 20.

are 2 to 4 kcal/mole lower (Ref. 23) than that for reaction 18. The pre-exponential factor is estimated to be 1/10 of gas kinetic; again a high estimate (about 5 times the experimental pre-exponential factors for reactions 19 and 20) was used to prevent underestimation of the exchange process.

III. IDENTIFICATION OF IMPORTANT PROCESSES

The more important processes in the HBr-NO two-photon system have been identified. The effects on the enrichment criteria α and β were observed by either 1) changing the rate constants or extinction coefficients associated with a process or 2) removing a process or group of processes from the model.

In general absorption processes have a greater effect on β , the absolute enrichment. Obviously the most important absorption processes are the absorption of the IR photon and dissociation of HBr($v=1$). No enrichment is possible without the IR photon and the dissociation of HBr($v=1$) leads to over 90 percent of the observed β . Dissociation of HBr($v=0$), however, does have a large effect on α ; for normal laser conditions the ground state dissociation, which slightly favors $H^{81}Br$, ($H^{79}Br$ is preferentially excited) leads to a 15-20 percent decrease in α .

Absorption of the IR and UV radiation have similar effects on β . Under non-saturation conditions an increase in the UV extinction coefficient is somewhat more effective in raising β than an increase in the IR coefficient. The IR transition is optically thick while the UV transition is optically thin. When the IR transition begins to saturate, the effect of IR absorption on β becomes even less. On the other hand α is generally only a function of the IR absorption. The isotopically specific IR absorption will increase the $H^{79}Br(v=1)/H^{81}Br(v=1)$ ratio and thus the ratio of $^{79}Br/^{81}Br$ that is dissociated. The UV absorption will not increase the ratio of dissociated $^{79}Br/^{81}Br$. In addition most of the important chemical reactions that can affect α are first order in dissociation products. Thus increased dissociation will increase both isotope exchange reactions (that lower α) and radical scavenging reactions (that maintain enrichment) by the same factor.

In general except for IR absorption, the kinetic processes have the greatest effect on α . At low HBr pressures ($\lesssim 1$ Torr) the chemical processes are more important while the energy transfer processes are more important at high HBr pressures ($\gtrsim 10$ Torr). The important energy transfer processes are second order in HBr while the important chemical processes are first order. Among the chemical processes, the

reaction $\text{Br} + \text{NO} + \text{M} \rightarrow \text{BrNO} + \text{M}$ has the most effect on β since NO is in excess. The reactions $\text{Br} + \text{BrNO} \rightarrow \text{Br}_2 + \text{NO}$ and $\text{Br} + \text{Br} + \text{M} \rightarrow \text{Br}_2 + \text{M}$, which are second order in Br, have a greater effect on β as the amount of dissociation is increased.

The chemical processes that have the most effect on α are $\text{H} + \text{HBr} \rightarrow \text{H}_2 + \text{Br}$ (reaction 12) and $\text{Br}^1 + \text{HBr} \rightarrow \text{Br} + \text{HBr}^1$ (reaction 16). These reactions have a greater influence on α than the processes $\text{Br}^1 + \text{Br}_2 \rightarrow \text{Br} + \text{Br}^1$ Br and $\text{Br}^1 + \text{BrNO} \rightarrow \text{Br} + \text{Br}^1 \text{NO}$ since the concentration of reactant HBr is much greater than that of the products, BrNO and Br_2 . In the basic model reaction 12 has a greater effect on enrichment than reaction 16. The collision frequency for H+HBr encounters is greater than that for Br+HBr. However, the gas kinetic pre-exponential factor and 6 kcal/mole activation energy for reaction 16 were only estimates. When a 1.4 kcal/mole activation was used instead, the dominant process was reaction 16; thus it is possible that reaction 16 actually dominates.

In general, the most important energy transfer processes are the V-V isotopic exchange reactions. These processes directly affect the ratio of excited H^{79}Br /excited H^{81}Br and thus influence both α and β . At high HBr pressures (about 10 Torr or above) these are the most important kinetic processes. At high NO/HBr ratios (about 100:1) the NO-HBr energy transfer rates become important, especially for β . The V-V and V-T reactions lower the concentration of vibrationally excited HBr; the results are similar to the effect of lowering the IR extinction coefficient.

IV. VARIATION OF EXTERNAL PARAMETERS

The enrichment is strongly affected by external parameters such as initial pressures, initial temperature, and intensities of IR and UV sources. Study of the variation of these parameters is in progress and preliminary results are available for variation of IR intensity, UV intensity, UV frequency, and initial pressures.

The variation of the excitation intensity of the IR and UV sources (at constant pulsewidth) has a substantial effect on the extent of enrichment. The absolute enrichment, β , varies linearly with the intensity of both the IR and UV sources (until saturation effects of the IR transition are observed). The enrichment ratio α increases with the intensity of the IR source but is nearly independent of the intensity of the UV source under the conditions used. Therefore, for conditions where saturation effects are absent, an increase in IR intensity rather than UV intensity will yield a more enriched product. When saturation effects are present the trade-off between increased α and increased β will determine the relative effectiveness of increasing the intensities of the two sources.

An increase in the frequency of the UV source (at constant photon density) increases β but decreases α . For example, as the wavelength of the UV source is changed from 265nm to 235nm, β is increased by a factor of seven while α is decreased by a factor of 2.5. In the spectral region where significant dissociation is possible, the extinction coefficient for $\text{HBr}(v=0)$ increases faster than that for $\text{HBr}(v=1)$, as frequency is increased. Thus, the optimum wavelength for the UV source will depend on trade-offs between the values of α and β and the photon density available at each wavelength.

Variation of initial reaction pressures substantially affects enrichment. Only preliminary results are available, but these indicate that both α and β decrease at high total pressures even if pressure broadening of the IR transition is ignored. This decrease in β as well as α implies that although chemical reactions can be the dominant kinetic processes at low pressures, enrichment is a stronger function of energy transfer processes.

The range of enrichment for the conditions that have been modeled are $\alpha = 0.1$ to 0.6 and $\beta \approx 10^{12} - 10^{13}$ molecules/cm³. The α values correspond to an increase in the ⁷⁹Br isotopic abundance of the products from 0.50 to about $0.55 - 0.80$. The β values represent $\sim 10^{-5}$ of the initial HBr concentration. These values should increase after optimization of the external parameters.

Other external parameters to be investigated are initial temperature, IR laser linewidth, excitation pulse width (including a simulation of cw sources), and the delay between the IR and UV pulses. The use of a broadband UV source and excitation of an IR overtone transition will also be modeled. Results from these studies will yield the range of conditions for which enrichment is possible and the optimization of those conditions.

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