A Reinvestigation of the Laser-Initiated Cl₂/HBr Chain Reaction: Absolute Rate Constants and the v = 2/v = 1 Ratio from Cl + HBr \rightarrow HCl(v) + Br

David A. Dolson[†] and Stephen R. Leone^{*}

Joint Institute for Laboratory Astrophysics, National Bureau of Standards and University of Colorado, and Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0440 (Received: January 26, 1987)

The Cl₂/HBr chain reaction is reinvestigated by using real time state-selected observations of $\Delta v = -1$ chemiluminescence from the HCl(v) products following pulsed laser photolysis of Cl_2 . These state-selected observations are analyzed with a more complete kinetic treatment to obtain room temperature rate constants for the chain propagation steps and the vibrational deactivation of HCl(v=1,2) by HBr. The chain propagation rate constants are $k_{R1} = (1.02 \pm 0.15) \times 10^{-11}$ and $k_{R2} = (1.12) \times 10^{-11}$ \pm 0.4) \times 10⁻¹⁵ cm³ molecule⁻¹ s⁻¹, respectively, for Cl + HBr $\frac{k_{BL}}{E}$ HCl(v) + Br and Br + Cl₂ $\frac{k_{BL}}{E}$ BrCl + Cl. Rate constants for vibrational deactivation of HCl(v=1) and HCl(v=2) by HBr are $k_{V1} = (1.06 \pm 0.16) \times 10^{-12}$ and $k_{V2} = (2.09 \pm 0.50)$ $\times 10^{-12}$ cm³ molecule⁻¹ s⁻¹. Relative intensity measurements of the HCl $v = 2 \rightarrow 1$ and $1 \rightarrow 0$ vibrational fluorescence are used to obtain an HCl(v) product branching ratio, $N_{v=2}/N_{v=1} = 0.40 \pm 0.06$. The kinetic analysis indicates that broad-band observations of infrared chemiluminescence may lead to erroneous rate constant determinations because of vibrational cascade, whereas the detection of individual vibrational states leads to correct results.

I. Introduction

The Cl + HBr \rightarrow HCl($v \le 2$) + Br reaction has been investigated in a number of infrared chemiluminescence studies¹⁻⁹ and classical kinetics measurements^{10,11} to obtain both the rate vibrational branching fractions and rate constant. Arrested relaxation experiments by Maylotte, Polanyi, and Woodall¹ provided the first HCl(v=2)/HCl(v=1) product branching ratio of 0.4. Later, Bergquist et al.² reported a branching ratio of 0.12 in a fast flow tube study, and Zwier et al.³ obtained a value of 0.11 from time-resolved infrared chemiluminescence observations in a laser-initiated reaction study. More recently Wickramaaratchi and Setser,⁴ using the fast flow technique with higher spectral resolution, measured a branching ratio of 0.37. Since the fast flow tube measurements^{2,4} agree regarding the HCl(v) distribution from Cl + HI, it is difficult to reconcile their difference for the Cl + HBr branching ratio. A detailed balancing calculation of Macdonald and Moore⁵ places a limit on the branching ratio of ≤ 0.07 . There is no compelling reason to suspect errors in any of the experimental results.

The Cl + HBr reaction rate constant has also been studied extensively. Moore and co-workers⁶⁻⁸ determined the rate constant and a non-Arrhenius temperature dependence from time-resolved infrared fluorescence measurements following the pulsed laser photolysis of Cl₂. Using a similar technique Nesbitt and Leone⁹ obtained the rate constants for the Cl + HBr reaction and the subsequent slower $Br + Cl_2$ reaction in their initial study of the Cl_2/HBr chain reaction system. The results of these investigations are all in good agreement, with a generally accepted value⁶ of (8.4 \pm 0.5) \times 10⁻¹² cm³ molecule⁻¹ s⁻¹ for Cl + HBr at room temperature. These experiments were conducted with various broad-band interference filters so that the observations are a weighted average of HCl $v = 1 \rightarrow 0$ and $v = 2 \rightarrow 1$ vibrational fluorescence. Rubin and Persky¹⁰ reported a slightly higher rate constant for Cl + HBr, 1.06×10^{-11} cm³ molecule⁻¹ s⁻¹, determined by a competitive method using mass spectrometry. They also observed an Arrhenius temperature dependence for this reaction over the range 222-504 K. Most recently, Lamb et al.¹¹ reported a very different rate constant of 3.4×10^{-12} cm³ molecule⁻¹ s⁻¹ using a very low pressure reactor, a value which falls far out of the range of the large body of data.

Several recent studies^{9,12-14} have emphasized the need for making vibrationally state-selected observations in infrared

chemiluminescence (IRCL) experiments when a distribution of product vibrational states occurs. The reason for this concern is that the vibrational deactivation rates for higher v levels can become competitive with the reaction rates for some chemical systems. In such systems the rise time of the product vibrational chemiluminescence may contain contributions from both the reaction of interest and the vibrational cascading process. Consequently, reaction rates extracted from rise time measurements based upon detection of multiple vibrational states may lead to erroneous results in some instances.

In this paper we report the results of a reinvestigation of the Cl_2/HBr chain reaction system. This study was undertaken in an attempt to reconcile the large discrepancy in the previous branching ratio measurements for the reaction of Cl atoms with HBr. In addition, the results provide a new determination of the Cl + HBr rate constant. Real time state-selected measurements of HCl(v=1) and (v=2) are recorded after pulsed laser initiation of the chain reaction in gas mixtures of Cl₂ and HBr diluted in argon. The observations are analyzed according to detailed solutions of the multiple state kinetics. The rate constant obtained for Cl + HBr is in good agreement with the value of Rubin and Persky,¹⁰ and the analysis indicates that the earlier IRCL reaction rate measurements⁶⁻⁹ are 20-30% low due to the influence of vibrational cascading. The much smaller rate constant result of Lamb, Kondo, and Benson¹¹ cannot be reconciled. The branching ratio (v = 2/v = 1) reported here (0.40) is in excellent agreement with the ~ 0.4 values obtained by arrested relaxation¹ and the flow tube experiment of Wickramaaratchi and Setser.⁴ Explanations for the lower literature values are discussed. There is still difficulty in reconciling this larger value of the branching ratio with the detailed balancing calculation using Macdonald and

- (1) Maylotte, D. H.; Polanyi, J. C.; Woodall, K. B. J. Chem. Phys. 1972, 57, 1547.
- (2) Berquist, B. M.; Bozzelli, J. W.; Dzelkalns, L. S.; Piper, L. G.; Kaufman, F. J. Chem. Phys. 1982, 76, 2972.
- (3) Zwier, T. S.; Bierbaum, V. M.; Ellison, G. B.; Leone, S. R. J. Chem. Phys. 1980, 72, 5426.
- (4) Wickramaaratchi, M. A.; Setser, D. W. J. Phys. Chem. 1983, 87, 64 $(A_{10} = 34.6 \text{ s}^{-1}).$
 - (5) Macdonald, R. G.; Moore, C. B. J. Chem. Phys. 1980, 73, 1681. (6) Mei, C.-C.; Moore, C. B. J. Chem. Phys. 1977, 67, 3936.
 - Bergmann, K.; Moore, C. B. J. Chem. Phys. 1975, 63, 643. (7)
 - (8) Wodarczyk, F. J.; Moore, C. B. Chem. Phys. Lett. 1974, 26, 484.
 (9) Nesbitt, D. J.; Leone, S. R. J. Chem. Phys. 1981, 75, 4949.

 - (10) Rubin, R.; Persky, A. J. Chem. Phys. 1983, 79, 4310.
 (11) Lamb, J. J.; Kondo, O.; Benson, S. W. J. Phys. Chem. 1986, 90, 941.
 - (12) Smith, I. W. M.; Wrigley, D. J. Chem. Phys. Lett. 1980, 70, 481.
 (13) Smith, I. W. M.; Wrigley, D. J. Chem. Phys. 1981, 63, 321.
 - (14) Dolson, D. A.; Leone, S. R. J. Chem. Phys. 1982, 77, 4009.

[†]This work was accomplished while D.A.D. was a NRC-NBS postdoctoral fellow. Current address: Department of Chemistry, The Ohio State University, Columbus, OH. *Staff Member, Quantum Physics Division, National Bureau of Standards,

Boulder, CO 80302.

Moore's⁵ rate constant for the reverse reaction of Br + HCl(v=2). The Cl₂/HBr chain reaction is one of the best documented cases to date of the influence of vibrational cascade deactivation upon reaction rate determinations. These results provide clear evidence that state-selected observations coupled with the proper kinetic analysis are crucial in the determination of reliable rate constants from real time vibrational chemiluminescence experiments.

II. Experimental Section

The experimental apparatus is essentially the same as that used in previous chain reaction investigations.¹⁴ It consists of a flow cell in which Cl_2 and HBr are diluted in a flow of argon (linear flow velocity = 15-80 cm s⁻¹) and irradiated with a pulsed ultraviolet laser to initiate the reactions. State-selected, real time infrared fluorescence from HCl(v=1) and (v=2) is detected with a fast infrared detector. The signals are digitized and signal averaged for 500-5000 laser pulses. The intensity vs. time curves are digitized and stored on floppy disks for subsequent computer analysis, and they are also plotted for manual data analysis.

Ultraviolet pulses at 355 nm (4-35 mJ, 5 ns) from the third harmonic of a Q-switched Nd:YAG laser generate Cl atoms at time = 0. The density can be varied over a wide range, 5×10^{11} cm⁻³ \leq [Cl]₀ \leq 5 \times 10¹³ cm⁻³; the atoms are produced in a 1-2.5-cm-diameter volume. Pseudo-first-order conditions are ensured by keeping [HBr]/[Cl]₀ > 30. The S/N values of the peak intensities are at least 20:1 after signal averaging and >40:1 for data used in the branching ratio measurements.

The Pyrex flow cell (4 cm diameter \times 40 cm long) is uniformly coated with a halocarbon wax to minimize wall-catalyzed reactions of Cl₂ + HBr. The Cl₂ and HBr reagents are added through separate nozzle inlets to the argon flow upstream of the photolysis region. Gas flow rates are adjusted with fine monel or stainless steel needle valves and measured by calibrated electronic flow meters. Reactant pressures are calculated from their partial flow rates and the total gas pressure, which is measured with a capacitance manometer. Linear flow velocities range from 15 to 80 cm s⁻¹ and the laser repetition rate is adjusted from 2 to 10 Hz to allow the reactants to be replenished between laser pulses.

A key ingredient in the measurement of the v = 2/v = 1branching ratio of the HCl(v) product and the accurate determination of the absolute rate coefficients is to separate the rotationally relaxed $v = 2 \rightarrow 1$ and $v = 1 \rightarrow 0$ emission with appropriate spectral filters. The time-dependent algebraic expressions for [HCl(v=2)] and [HCl(v=1)] developed in the next section are then used to analyze these state-selected observations. Three types of spectral filters are used to provide vibrational state specificity in these experiments. The most important of these is a cold gas filter containing 25 kPa of HCl (1 Pa = 7.5×10^{-3} Torr) in a 1-cm optical path. One measurement is made with the HCl frozen in a cold finger by liquid nitrogen. This first observation is the sum of the $v = 2 \rightarrow 1$ and $1 \rightarrow 0$ emission signals. A second observation is made with the cold finger at room temperature so that the $1 \rightarrow 0$ emission is absorbed, but the 2 \rightarrow 1 fluorescence is transmitted. After normalization for the laser energy between the two observations, the digitized data files are subtracted to obtain the $1 \rightarrow 0$ emission signal. A broad-band interference filter (50% T points at 3210 and 2480 cm⁻¹; 10% T points at 3260 and 2400 cm⁻¹) is used to restrict the spectral observation in the general region of the HCl emission. The third filter is a cold gas filter containing 27 kPa of HBr in a 5.1-cm path, used to remove the HBr $1 \rightarrow 0$ fluorescence that occurs by vibrational energy transfer from the HCl(v) species.

The ratio of HCl $2 \rightarrow 1$ and $1 \rightarrow 0$ emission intensity, $I(2\rightarrow 1)/I(1\rightarrow 0)$, is converted into a ratio of the v = 2 and v = 1 populations, [HCl(v=2)]/[HCl(v=1)]. This is accomplished with a knowledge of the relative detection efficiency of the filtered InSb detector. The 77 K photovoltaic detector (1.48-cm² active surface area) exhibits a flat response per photon over the spectral range of the HCl $2 \rightarrow 1$ and $1 \rightarrow 0$ emission. If a Boltzmann distribution of population is assumed among the rotational levels, the emission intensity from a vibrational level, v', that is recorded by the detector, is given by

$$I(v' \rightarrow v'') \propto \sum_{J'} \frac{N_{v'}(J')}{(2J'+1)} \nu^3 |R_{v'J'}^{v(J')}|^2 T_{J'}$$

where T_{ν} is the frequency-dependent filter transmittance, $|\mathcal{R}_{\nu'J'}^{vJ'}|$ is the transition moment for a particular $v', J' \rightarrow v'', J''$ transition, and

 $N_{v'}(J') \propto B_{v'}(J' + J'' + 1) \exp[-B_{v'}J'(J' + 1)/kT]$

The calculations are performed using the molecular constants of Rank et al.¹⁵ and the corrected transition moments given in ref 4. The T_{ν} values of the broad-band filter are obtained from a transmission spectrum taken with a spectrometer. The result is given by

$$\frac{[\text{HCl}(v=2)]}{[\text{HCl}(v=1)]} = 0.625 \frac{I(2 \rightarrow 1)}{I(1 \rightarrow 0)}$$

The value, 0.625, is very near to the ratio of the Einstein coefficients, ${}^{4}A_{10}/A_{21} = 0.582$, which indicates that the filter transmission is relatively flat over the region of interest.

All gases are handled in a conventional glass vacuum line with $<1.3 \times 10^{-3}$ Pa background pressure. Argon (99.999%) is used directly from a gas cylinder, while the Cl₂ (99.5%) is vacuum distilled at a slush bath temperature corresponding to approximately 1 kPa vapor pressure. The middle fractions from the distillations are stored in 12-L Pyrex bulbs and the Cl₂ is pumped on for 1 to 10 minutes while being held at 147 K (1-propanol slush) to remove possible CO₂ impurity. These samples are thoroughly degassed before each use, and during the experiments their vapor pressure is maintained at ~30 kPa over the liquid to ensure constant backing pressures. The needle valves require infrequent adjustment during the course of several experiments to maintain a constant gas flow. Cl₂ is used without distillation (99.9%) when high flow rates are required. These samples are degassed several times at 77 K and then at 147 K for CO₂ removal.

The HBr used in this study is prepared by passing an approximately 2:1 mixture of H₂ (99.999%):Br₂ (99.8%) at ~1-10 kPa through a 12-mm quartz tube heated to ~600 °C in a tube furnace. The HBr product is collected together with a small amount of unreacted Br₂ in a 77 K cold finger. Repeated vacuum distillations are used to remove the Br₂ impurity. Preliminary results using commercially available HBr yielded a slower rise time for the 1 \rightarrow 0 emission than for the 2 \rightarrow 1 emission. Concern that this indicated a potential impurity, possibly HI, prompted this synthesis of HBr from high-purity H₂ and Br₂. Both HBr samples gave the same results. As will be shown below the slower 1 \rightarrow 0 rise time was subsequently determined to be a result of vibrational cascading from the v = 2 level.

III. Kinetic Analysis

A. Rate Coefficients. The following reactions and vibrational energy transfer processes are included in the two-state (v = 1 and v = 2) kinetic analysis developed in this section:

(initiation)
$$Cl_2 \xrightarrow{355 \text{ nm, 5 ns}} 2Cl$$

Cl + HBr
$$\xrightarrow{\kappa_{Rl}}$$
 HCl($v \le 2$) + Br, $\Delta H^{\circ}_{298} = -65.0 \text{ kJ mol}^{-1}$ (R1)

$$Br + Cl_2 \xrightarrow{k_{R_2}} BrCl + Cl, \quad \Delta H^{\circ}_{298} = +24.1 \text{ kJ mol}^{-1} \quad (R2)$$

$$HCl(v=1) + HBr(v=0) \xrightarrow{\sim_{V_1}} HCl(v=0) + HBr(v=1) + 327 \text{ cm}^{-1} (3.9 \text{ kJ mol}^{-1}) (V1)$$

k ...

$$\begin{array}{c} \text{HCl}(v=2) + \text{HBr}(v=0) \xrightarrow{k_{V_2}} \\ \text{HCl}(v=1) + \text{HBr}(v=1) + 223 \text{ cm}^{-1} (2.7 \text{ kJ mol}^{-1}) (V2) \end{array}$$

Reactions R1 and R2 constitute the chain reaction with a rapid

⁽¹⁵⁾ Rank, D. H.; Rao, B. S.; Wiggins, T. A. J. Mol. Spectrosc. 1965, 17, 122.

Laser-Initiated Cl₂/HBr Chain Reaction

first step followed by a much slower regeneration of the Cl atoms. Termination reactions, such as recombination of the chain carriers, Br and Cl, are omitted because of the small concentrations of these species and the short time scale of the experimental observations. The HCl(v) species deactivate almost exclusively by one-quantum vibrational energy transfer to HBr(v=0).¹⁶ Deactivation of HCl(v) by Ar, Cl₂, Cl, and Br is not important due to the small rate constants with Ar and Cl₂ and the small concentrations of Br and Cl atoms.

The appropriate differential equation is solved under pseudofirst-order conditions, $[HBr] \gg [Cl]$ and $[Cl_2] \gg [Br]$, to yield

$$[Cl] = \frac{k_{R1}[HBr][Cl]_0}{k_{R1}[HBr] + k_{R2}[Cl_2]} \exp[-(k_{R1}[HBr] + k_{R2}[Cl_2]]t] + \frac{k_{R2}[Cl_2][Cl]_0}{k_{R1}[HBr] + k_{R2}[Cl_2]} (1)$$

where $[Cl]_0$ is the initial Cl atom concentration at time = 0 produced by the photolysis laser. This expression indicates that [Cl] decays to a steady-state value, $[Cl]_{ss}$, given by the second term of eq 1. The decay rate of Cl atoms is given by the *sum* of the two chain propagation rates.

The expressions for [HCl(v=2)] can be obtained for two distinct experimental conditions, set by the concentration of $[Cl_2]$ relative to [HBr]. One simplification is achieved for $k_{R1}[HBr] \gg k_{R2}[Cl_2]$. At the highest $[Cl_2]$ used in this study, $k_{R1}[HBr]$ is at least two orders of magnitude greater than $k_{R2}[Cl_2]$. Thus using eq 1 and making approximations allowed in this case, we can find for the HCl(v=2) product:

$$[HCl(v=2)] \simeq [HCl(v=2)]_0 \{ \exp(-k_{V2}[HBr]t) - \exp(-k_{R1}[HBr]t) \} + [HCl(v=2)]_{ss} \{ 1 - \exp(-k_{V2}[HBr]t) \}$$
(2)

where

$$[\text{HCl}(v=2)]_0 \simeq \frac{k_{\text{Rl}}\alpha[\text{Cl}]_0}{k_{\text{Rl}} - k_{\text{V2}}}$$
(3)

$$[\mathrm{HCl}(v=2)]_{\mathrm{ss}} \simeq \frac{k_{\mathrm{R2}}[\mathrm{Cl}_2]\alpha[\mathrm{Cl}]_0}{k_{\mathrm{V2}}[\mathrm{HBr}]} \tag{4}$$

and α is the fraction of [Cl]₀ that yields the HCl(v=2) product.

The kinetic behavior of [HCl(v=2)] described by eq 2 is displayed in the experimental data of Figure 1. Upon generation of $[Cl]_0$ at time = 0, HCl(v=2) is produced in reaction R1, and the $2 \rightarrow 1$ emission signal rises quickly with an exponential time constant, $\tau_{rise} = (k_{R1}[HBr] + k_{R2}[Cl_2])^{-1} \simeq (k_{R1}[HBr])^{-1}$. After a few intervals of the time duration, τ_{rise} , the concentration of [Cl] approaches $[Cl]_{ss}$, and the rate of HCl(v=2) production decreases to the linear term αk_{R1} [HBr][Cl]_{ss}. Vibrational deactivation of HCl(v=2), primarily by V-V transfer to HBr, leads to an exponential decay of the v = 2 signal with time constant, $\tau_{V2} \simeq$ $(k_{V2}[HBr])^{-1}$. The signal intensity drops to a nonzero steady-state level, I_{ss} , proportional to $[HCl(v=2)]_{ss}$. This small, steady-state signal, which is only readily observed at relatively high [Cl₂], is the signpost of the slow chain propagation step that converts Br atoms back into Cl atoms. The exponential decay of HCl(v=2), when extrapolated back to time = 0, yields a signal intensity, I_0 \propto [HCl(v=2)]₀. The rate coefficients, k_{R1} and k_{V2} , are obtained directly from the real time signal rise and decay, respectively, while k_{R2} is determined from the ratio, $I_{ss}/I_0^{.9,14}$

Experiments with the highest concentrations of [Cl₂], described by eq 2-4, are used primarily for k_{R2} determination, where a measurable I_{ss} must be generated. Most of the other experiments considered here are carried out with ten- to twentyfold lower [Cl₂], where, in addition to the previous k_{R1} [HBr] $\gg k_{R2}$ [Cl₂] condition, the relationships k_{V2} [HBr] $> k_{V1}$ [HBr] $\gg k_{R2}$ [Cl₂] also apply.¹⁶ This allows for an even greater simplification of eq 2

 $[HCl(v=2)] \simeq$

$$[HCl(v=2)]_{0} \{ \exp(-k_{V2}[HBr]t) - \exp(-k_{R1}[HBr]t) \}$$
(5)



Figure 1. Time-resolved infrared fluorescence from HCl(v=2) produced in reaction R1. The signal is described by eq 4 where $I_0 \equiv [HCl(v=2)]_0$ and $I_{ss} \equiv [HCl(v=2)]_{ss}$.

where $[\text{HCl}(v=2)]_0$ is still given by eq 3. Here the steady-state signal indicative of reaction R2 is negligible and is no longer observable at lower chlorine concentrations. The values of k_{R1} and k_{V2} are still determined from the signal rise and decay times, but the chain behavior is suppressed so that the v = 2/v = 1 product branching ratio is more easily determined.

In the absence of the chain reaction the HCl(v=1-0) signal is proportional to

$$[\text{HCl}(v=1)] \simeq [\text{HCl}(v=1)]_0 \{\exp(-k_{V1}[\text{HBr}]t) - \exp(-k_{R1}[\text{HBr}]t)\} + [\text{HCl}(v=1)]_{vv} \{\exp(-k_{V1}[\text{HBr}]t) - \exp(-k_{V2}[\text{HBr}]t)\}$$
(6)

where

$$[\text{HCl}(v=1)]_0 \simeq \left[\frac{k_{\text{R1}}[\text{Cl}]_0}{k_{\text{R1}} - k_{\text{V1}}} \right] \left[\beta - \frac{k_{\text{V2}}}{k_{\text{R1}} - k_{\text{V2}}} \alpha \right]$$
(7)

$$[\text{HCl}(v=1)]_{vv} \simeq \frac{k_{V2}k_{R1}\alpha[\text{Cl}]_0}{(k_{V2}-k_{V1})(k_{R1}-k_{V2})}$$
(8)

and β is the fraction of [Cl]₀ that yields HCl(v=1). The first term in eq 6 is much like eq 5; however, the expression for $[HCl(v=1)]_0$ has an additional term containing α , the branching fraction into v = 2, which is introduced by vibrational cascading. The second term in eq 6 is due to the V-V production of HCl(v=1) described by reaction V2. According to eq 6, with $k_{R1} > k_{V2} > k_{V1}$, an additional signal in HCl(v=1) rises with the same time constant with which [HCl(v=2)] decays, τ_{V2} , adding a third time component to the $1 \rightarrow 0$ signal. The relative influence of this term on the overall kinetic behavior of [HCl(v=1,t)] is dependent on the branching ratio into v = 2. In the limit, $\alpha \rightarrow 0$, the HCl(v=1) population is described by the first term in eq 6, and in this limit the rise time is simply related to $k_{\rm R1}$ by $\tau_{\rm rise} \simeq (k_{\rm R1} [\rm HBr])^{-1}$. If $\alpha \neq 0$ the rising intensity of the 1 \rightarrow 0 emission is not single exponential, and an analysis that assumes a single risetime may lead to erroneous determinations of k_{R1} . The seriousness of the error increases with increasing ratio of α/β . The complication of the vibrational cascading leads to the conclusion that k_{R1} can be best determined from the state-selected observations of the 2 ▶ 1 emission. An examination of eq 6 reveals that extrapolation of the exponential decay to time = 0 is proportional to the sum,



Figure 2. Calculated HCl $v = 1 \rightarrow 0$ emission curves obtained by using eq 11. The inset time scale has been expanded fivefold, and the intensity scale has been compressed by a factor of two in order to show the early time detail of the signals. A visual inspection reveals that there are at least three time components to the upper curve. The lower curve gives no visible hint of a third time component although it is present. The parameters for the lower curve were chosen to approximate the HCl(v=1) signal in the Cl + HBr reaction.

 $[\text{HCl}(v=1)]_0 + [\text{HCl}(v=1)]_{\text{vv}}$. The value of k_{V1} is determined directly from the measured signal decay time, $\tau_{V1} \simeq (k_{V1}[\text{HBr}])^{-1}$. Equation 6 can be restated as

$$[\text{HCl}(v=1)] \simeq (A + B) \exp(-t/\tau_{V1}) - A \exp(-t/\tau_{V2}) - B \exp(-t/\tau_{R1}) (9)$$

by equating A with $[HCl(v=1)]_{vv}$ and B with $[HCl(v=1)]_0$. In certain limits, it might be possible to identify the three time components of eq 9 in the experiment. However, in our case the experimental observations appear to be a single exponential rise followed by a single decay. Two extremes are illustrated in Figure 2 with computer-generated $1 \rightarrow 0$ emission signals calculated by using eq 9. The upper trace is calculated for τ_{V1} : τ_{V2} : $\tau_{R1} = 100:20:1$ and A/B = 1.37 (corresponding to a branching ratio, α/β , = 1). Here, the time constants are considerably different, and A/B is large enough so that two components in the rise time are easily identified. The lower trace of Figure 2 also obeys eq 9, with $\tau_{V1}:\tau_{V2}:\tau_{R1} = 100:52:11$ and A/B = 0.77 (corresponding to α/β 0.3. This curve appears to rise smoothly with a single exponential time constant, and even if curves of this type are subjected to fitting procedures to obtain three time constants, the results may not be reliable. A significant error occurs if this curve is fit to the difference of two exponentials by taking the "rise time" to be τ_{R1} (i.e. neglecting vibrational cascading and considering only the first term in eq 6). It is possible to obtain respectable correlation coefficients from such a fit, and although the value found for τ_{V1} is quite good, " $\tau_{\rm rise}$ " is about twice as large as the true $\tau_{\rm R1}$ in this example. In the following section we will show that this effect upon " τ_{rise} ", while devastating to obtain k_{R1} , provides a means to measure the v = 2:v = 1 product branching ratio reliably.

The preceding example and discussion illustrates the potential problems in attempting to extract k_{R1} from rise time observations where vibrational cascading may interfere. It is more rigorous to obtain k_{R1} from state-selected observations on the highest product vibrational level, which is produced only by reaction. Previous investigations of reaction R1 have been accomplished with broad-band fluorescence detection of both excited levels and by fitting the signals as a simple difference of two exponential terms.⁶⁻⁹ In reality, the observations consist of the sum of one signal obeying eq 5 plus one signal described by eq 6, with a weighting factor determined by the branching ratio, the spontaneous emission coefficients, and the optical filter characteristics. This problem has led to rate constant determinations that are 20–30% too low in previous reports.

B. Branching Ratio. Measurements of the state-selected $v = 2 \rightarrow 1$ and $v = 1 \rightarrow 0$ emission signals, after normalization for



Figure 3. Apparent reaction rate constants obtained from calculated 1 $\rightarrow 0$ emission curves. The curves were calculated for various values of α/β by using eq 11 with $k_{\rm R1} = 10.0$, $k_{V2} = 2.1$, and $k_{V1} = 1.1$ (× 10⁻¹² cm³ molecule⁻¹ s⁻¹). Rise times were obtained by the same treatment used for the experimental observations, and the "apparent $k_{\rm R1}$ " is $\tau_{\rm rise}^{-1}$ divided by the value of [HBr] used in the calculation. "Apparent $k_{\rm R1}$ " values from experimental 1 $\rightarrow 0$ observations are used with this plot to provide an estimate for α/β . The arrows indicate the limiting values at low and high values of α/β .

laser energy, are analyzed with the kinetics equations to obtain α/β , the v = 2:v = 1 product branching ratio of reaction R1. Two very different approaches may be used to obtain α/β from the experimental observations. The more obvious method involves measurement of the relative intensities of the v = 2 and v = 1 fluorescence signals, taking account of the vibrational cascade, and conversion of the intensity ratio to the population ratio using the relationship for the filter and radiative factors given earlier

$$\frac{[\text{HCl}(v=2)]}{[\text{HCl}(v=1)]} = 0.625 \frac{I(2 \to 1)}{I(1 \to 0)}$$
(10)

A less obvious method to determine α/β involves the effect of the branching ratio and vibrational cascading upon the rise time of the $1 \rightarrow 0$ signal. The details of this latter estimate are presented first, followed by a discussion of the more rigorous method based upon eq 10.

In the discussion of the rate coefficients above, we presented a calculated $1 \rightarrow 0$ emission signal for the case $\alpha/\beta = 0.3$. When this signal is analyzed as if it were a single potential rise, the "rise time" is about twice as long as the real τ_{R1} . Similar $1 \rightarrow 0$ signals can be generated by using eq 6 with different values of α/β . Figure 3 displays the relationship between the apparent k_{R1} from the 1 \rightarrow 0 "rise times" and the branching ratio. Because these signals really have two time components in the rise, a simple fitting procedure will yield a "rise time" that is sensitive to the specific time region used in the analysis. If similar time regions are used for the simulated signals and for the experimental $1 \rightarrow 0$ observations, Figure 3 can be used to obtain an estimate of the branching ratio. A unique aspect of this method is that only v $= 1 \rightarrow 0$ state-selected observations are required. There is no need to know the relative HCl(v=2) and HCl(v=1) detection efficiencies. However, all the rate constants, k_{R1} , k_{V1} , and k_{V2} , must be separately determined in different limits.

The intensity ratio method uses eq 10, in which eq 5 and 6 are substituted for the numerator and denominator, respectively. In general, experimentally determined values for k_{R1} , k_{V2} , and k_{V1} can be used to evaluate the left-hand side of eq 10 at specific times, t, at which the intensity ratio has been measured. Since the entire emission waveforms are experimentally obtained, $I(2\rightarrow 1)$ and $I(1\rightarrow 0)$ can be taken at any respective times t_2 and t_1 without a restriction that $t_1 = t_2$. Thus peak intensities, which can be determined with minimal uncertainty at times $t_1 > t_2$, may be used to determine the branching ratio.

The intensity ratio can also be determined in two limiting cases.

TABLE I: Rate Coefficients in the Cl₂ + HBr Chain Reaction System

expt no. ^a	P _{HBr} ^b	$P_{\text{Cl}_2}^{\ b}$	P _{Ar} ^b	$k_{\mathbf{R}1}^{c}$	k_{R2}^{d}	k _{v2} ^c	k_{V1}^{c}	apparent $k_{R1}^{c,e}$
1	8-43	25	630	9.5		2.61	1.15	5.4 (0.32)
2	8-31	25	600	9.7		2.16		
3	5-32	15	710	11.0		1.95		
4	7-37	15	710	9.8		1.96	1.01	5.7 (0.28)
5	4-25	12	630	11.3		2.07	1.01	4.9 (0.41)
6	8-43	264	660	10.5	1.1	1.99		
7	7-43	287	620	9.4		1.86		
			av ±2 σ^{f}	10.2 ± 1.5	1.1 ± 0.4^{g}	2.09 ± 0.50	1.06 ± 0.16	

^a Experiments consist of 7-17 measurements of $1 \rightarrow 0$ and/or $2 \rightarrow 1$ signals over a range of HBr pressures. ^b Pascal (1 Pa = 7.5 × 10³ Torr). ^c 10⁻¹² cm³ molecule⁻¹ s⁻¹. ^d 10⁻¹⁵ cm³ molecule⁻¹ s⁻¹. ^e From $1 \rightarrow 0$ observations (values in parentheses are estimates of α/β from Figure 3). ^f Standard deviations of the individual determinations are less than the quoted standard deviation about the mean. ^g Estimated standard deviation.

In one, the intensities are obtained by back-extrapolating the signal decays to t = 0 and used with the expression:

$$\frac{[\text{HCl}(v=2)]_0}{[\text{HCl}(v=1)]_0 + [\text{HCl}(v=1)]_w} = 0.625 \frac{I^0(2 \to 1)}{I^0(1 \to 0)} \quad (11)$$

It is also possible to measure the intensity ratio in the earliest part of the signal rises near t = 0 where vibrational deactivation is not yet important. In this case the branching ratio is given by

$$\frac{\alpha}{\beta} = 0.625 \frac{I(2 \to 1)}{I(1 \to 0)} \tag{12}$$

where a simplification of eq 10 is made by using the approximation, $e^{-kt} \simeq 1 - kt$. The results obtained by using each of these approaches will be compared in the next section.

IV. Results and Discussion

A. Rate Coefficients from HCl(v=2) Observations. The state-selected HCl(v=2) observations provide the best opportunity to measure $k_{\rm Rl}$. Under conditions of high [Cl₂], the 2 \rightarrow 1 emission obeys eq 2 and k_{R2} may also be obtained. Figure 1 presents a typical $2 \rightarrow 1$ emission signal viewed through both the HCl and HBr cold gas filters and the interference bandpass filter. The steady-state intensity, $I_{ss} \propto [\text{HCl}(v=2)]_{ss}$, is obtained at $t \gg$ $\tau_{V2} \simeq (k_{V2}[HBr])^{-1}$ to minimize any contribution from the first term of eq 2. The decaying signal intensity (before I_{ss} is reached) is subjected to a semilog least-squares fit in order to obtain $\tau_{\rm V2}$ and $I_0 \propto [\text{HCl}(v=2)]_0$. The difference between the back-extrapolated decay and the signal rise is subjected to a semilog fit to obtain τ_{rise} . Three quantities are obtained from an analysis of the 2 \rightarrow 1 emission observations with high [Cl₂]: τ_{V2} , τ_{rise} , and the ratio, (I_{ss}/I_0) . At lower [Cl₂] the slow chain behavior is suppressed, and $(I_{\rm ss}/I_0) \sim 0$; however, $\tau_{\rm V2}$ and $\tau_{\rm rise}$ are still obtained by the semilog fitting procedures described.

In a typical experiment $[Cl_2]$ and [Ar] are held approximately constant while emission signals are collected at varying HBr pressures. The measured time constants for the rise and decay of the $2 \rightarrow 1$ emission are related to the rate constants by τ_{rise} $\simeq (k_{R1}[HBr])^{-1}$ and $\tau_{V2} \simeq (k_{V2}[HBr])^{-1}$, respectively. Plots of τ_{V2}^{-1} and τ_{rise}^{-1} vs. [HBr] yield the respective rate constants k_{V2} and k_{R1} from the slopes of linear least-squares fits of the data. Plots of representative data are displayed in Figures 4 and 5 for one experiment at low [Cl₂]. The values of k_{R1} and k_{V2} obtained from these plots are listed in Table I along with results from six other experiments.

The average value $(\pm 2\sigma)$ of k_{R1} from Table I is $(1.02 \pm 0.15) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. This is ~20% higher than the result of Mei and Moore⁶ and should be considered as more accurate since the interference due to vibrational cascading is not present in the 2 \rightarrow 1 observations. The recent flow tube result of Rubin and Persky,¹⁰ $k_{R1} = 1.06 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹, is based upon a competitive rate technique using C₂H₆ as the reference reactant and mass spectrometric measurements of the HBr and C₂H₆ removal. Their value is also free from vibrational cascading interference, and it is in excellent agreement with our determination. Lamb et al. report a value of $k_{R1} = 3.4 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ in a recent investigation using an improved very low pressure reactor (VLPR).¹¹ Considering the good agreement of previous IRCL results,⁶⁻⁹ the improved understanding provided



Figure 4. State-selected vibrational deactivation rates vs. [HBr]. The slope of the least-squares fit gives the rate constant for vibrational relaxation of HCl(v) by HBr.



Figure 5. Reaction rate for (R1) vs. [HBr] from HCl $2 \rightarrow 1$ rise time measurements. k_{R1} is the slope of the line through the v = 2 data. Data for v = 1 were obtained as described in the text. Vibrational cascading slows the "rise time" for the $1 \rightarrow 0$ signal, thereby providing a novel method by which to measure the HCl(v=2)/HCl(v=1) branching ratio, but yielding an incorrect determination of k_{R1} .

by the present state-selected study, and the confirmation of the competitive rate results,¹⁰ it would seem that the VLPR result has significantly underestimated k_{R1} . The VLPR experiment is performed under conditions far from pseudo-first-order and does not consider the effects of back reaction Br + HCl(v=2) \rightarrow HBr + Cl; however, this would only seem to increase the observed rate of Cl removal as Br and HCl(v=2) are formed. Thus there is no way to reconcile the VLPR results.

Rubin and Persky¹⁰ found that $k_{R1}(T)$ obeys the Arrhenius expression, while Mei and Moore⁶ observed a distinct curvature in their Arrhenius plot, and Lamb et al.¹⁶ found no T dependence



Figure 6. Plot of steady-state intensity ratio data from $2 \rightarrow 1$ observations at high $[Cl_2]$ (see Figure 1 for example). According to eq 13 the slope of the line is k_{R2} . The different symbols represent results from two separate sets of experiments.

over a smaller range of temperatures. The disagreement between the results of ref 6 and 10 may be due, in part, to an undetected vibrational cascading interference in the IRCL study, reasoned as follows.⁶ Quasi-classical trajectory calculations predict an increase in α/β with T.¹⁷ Figure 3 indicates that, as α/β increases, the apparent $k_{\rm R1}$ is reduced (for the 1 \rightarrow 0 component to the signal) due to the increasing contribution of vibrational cascading. The net effect upon the experimental observations depends upon the values of $k_{\rm R1}$ and the increase in α/β , and upon the interference filter used. Consequently, we can only suggest that the true $k_{RI}(T)$ behavior may have been obscured by vibrational cascading in the broad-band IRCL observations.⁶ This effect may be more severe in the Cl + HI reaction, which populates HCl up to v = 4.

Vibrational relaxation of HCl(v=2) is almost entirely due to process V2, as discussed in the kinetic analysis section. Results from plots such as in Figure 5 are summarized in Table I for all seven experiments. The average value for k_{v_2} is (2.09 ± 0.50) $\times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ and is in agreement with the only other measured value,¹⁸ (2.9 \pm 0.4) \times 10⁻¹², at the $\pm 2\sigma$ uncertainty limits of each value.

While the temporal behavior of the $2 \rightarrow 1$ emission is governed primarily by k_{R1} and k_{V2} , the I_{ss}/I_0 intensity ratio provides a measurement of k_{R2} . The slow propagation reaction R2 that regenerates Cl atoms was previously studied in this group,⁹ but without vibrational state-selective observations because the HCl(v=2) population was thought to be low.³ In the present study, the value of k_{R2} is determined from the HCl $v = 2 \rightarrow 1$ observations in order to avoid complications from vibrational cascading. Equations 3 and 4 are combined to yield

$$I_{\rm ss}/I_0 \simeq k_{\rm R2}[{\rm Cl}_2](\tau_{\rm V2} - \tau_{\rm rise})$$
 (13)

In two sets of experiments [Cl₂] was increased by ten- to twentyfold over the lower [Cl₂] experiments in order to generate measurable I_{ss} levels. A plot of the intensity ratio vs. $[Cl_2](\tau_{V2})$ $-\tau_{rise}$) for these two sets of experiments appears in Figure 6. A linear fit of the data yields $k_{R2} = (1.1 \pm 0.4) \times 10^{-15} \text{ cm}^3 \text{ mol-}$ ecule⁻¹ s⁻¹ as the slope, where the uncertainty is estimated from both the scatter and the errors in τ_{v_2} and τ_{rise} . This value is in general agreement with the previous measurement, $9(2.4 \pm 0.4)$ \times 10⁻¹⁵ cm³ molecule⁻¹ s⁻¹, although there is no simple reason why the results should differ. Thermodynamic data for reaction R2 yields $\Delta G = 21.9 \pm 1.3 \text{ kJ/mol}$ at 298 K.¹⁹ When the measured rate constant for the reverse reaction $Cl + BrCl \rightarrow Br + Cl_2$ is used,²⁰ (1.45 \pm 0.2) \times 10⁻¹¹ cm³ molecule⁻¹ s⁻¹, the detailed

(17) Brown, J. C.; Bass, H. E.; Thompson, D. L. J. Phys. Chem. 1977, 81, 479



Figure 7. $2 \rightarrow 1$ and $1 \rightarrow 0$ emission from HCl(v) in (R1). The $1 \rightarrow 0$ 0 signal is obtained by subtracting the $2 \rightarrow 1$ curve from the total emission curve as described in the text. The $2 \rightarrow 1$ curve has been shifted by 40 μ s for this presentation. These curves are the result of 5000 laser shots using the HCl cold gas filter $(2 \rightarrow 1)$ and 5000 shots without the HCl filter $(2 \rightarrow 1 \text{ and } 1 \rightarrow 0)$. Branching ratio data are obtained from emission curves of this quality.

balancing prediction for k_{R2} is $(2.2^{+1.4}_{-0.9}) \times 10^{-15}$ cm³ molecule⁻¹ s⁻¹, where the uncertainty is obtained from the uncertainty in ΔG . This prediction is in reasonable agreement with our value of k_{R2} .

B. Rate Coefficients from HCl(v=1) Observations. Signals from HCl $v = 2 \rightarrow 1$ and $v = 1 \rightarrow 0$ are displayed in Figure 7 for low $[Cl_2]$ where the slow chain behavior is suppressed. Both curves have been obtained by using the same experimental conditions and are displayed on the same scale. The lower $2 \rightarrow 1$ curve has been shifted by 40 μ s so that overlap at early times is avoided. The upper curve in this figure is the $1 \rightarrow 0$ emission signal obtained by the subtraction technique discussed above. Although the $v = 1 \rightarrow 0$ curve appears to be a simple difference of two exponential terms, this appearance is deceptive, since it actually contains the three terms of eq 9. The two time constants in the rising portion of this signal are not separable by our semilog fitting procedures. Unsuccessful attempts were made to subject the $1 \rightarrow 0$ emission curves to a nonlinear least-squares fitting procedure using eq 9. Consequently, the only reliable rate constant information that can be obtained from the HCl $1 \rightarrow 0$ observations is for $\tau_{\rm V1}$.

In order to avoid cascading interference in the measurement of τ_{V1} , the semilog fitting procedure is made at a time, $t \ge 5\tau_{V2}$. This requirement forces the τ_{V1} fit to occur in a region of low intensity. The experimentally determined τ_{V1} values are plotted as τ_{V1}^{-1} vs. [HBr] in Figure 4, and k_{V1} is obtained from the slope of the best linear fit. The results of the three measurements of k_{V1} are listed in Table I, and the average value is $k_{V1} = (1.06 \pm 0.16) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This value is in excellent agreement with the range of literature values, $^{16}(1.0-1.2) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹.

Rise times were also obtained from HCl $v = 1 \rightarrow 0$ curves in the same manner in which the τ_{rise} values were obtained from the $2 \rightarrow 1$ curves. These values provide "time constants" that are useless for obtaining k_{R1} ; however, the apparent k_{R1} generated by this procedure is useful in estimating the v = 2/v = 1 branching ratio of reaction R1. A plot of these data is also included in Figure 5 along with the reliable data from the v = 2 observations. The apparent value of k_{R1} is in large error from these data. The greater scatter in these $v = 1 \ "\tau_{rise}"$ data is likely to be due to the errors associated with fitting a single exponential, which does not correctly describe the $1 \rightarrow 0$ emission. However, similar plots of other $1 \rightarrow 0$ experimental data can have a very good appearance, yielding good correlation coefficients, $r^2 > 0.99$. Thus, one cannot rely completely upon the quality of fitting to indicate unsound interpretations of the kinetic data. The "apparent k_{R1} " values determined in three experiments are listed in Table I.

C. HCl(v=2)/HCl(v=1) Branching Ratio. The "apparent k_{R1} " values obtained from HCl $1 \rightarrow 0$ "rise time" measurements provide

⁽¹⁸⁾ Dasch, C. J.; Moore, C. B. J. Chem. Phys. 1980, 72, 4117.
(19) JANAF Thermochemical Tables, 2nd ed.; National Bureau of Standards: Washington, DC, 1971; NSRD-NBS No. 37.
(20) Clyne, M. A. A.; Cruse, H. W. J. Chem. Soc., Faraday Trans. 2

^{1972, 68, 1377.}

a novel method by which the branching ratio, $\alpha/\beta = [\text{HCl}(v=-2)]/[\text{HCl}(v=1)]$, can be estimated. This method, presented in section III.B, is based on the fact that the contribution of vibrational cascading to the $1 \rightarrow 0$ "rise time" increases with α/β . Consequently, the "apparent k_{Rl} ", obtained from an analysis of the rise as a single exponential, decreases as α/β increases. This relationship is summarized quantitatively in Figure 3. The three "apparent k_{Rl} " values of Table I, in conjunction with Figure 3, yield an average value of $\alpha/\beta = 0.34$.

Measurements of [HCl(v=2)]/[HCl(v=1)] from intensity ratios lead to a more direct determination of α/β . Such measurements require that both the $2 \rightarrow 1$ and total emission amplitudes be obtained under the same experimental conditions. The $1 \rightarrow 0$ signal is obtained by the subtraction technique discussed earlier. The results presented here are from experiment 5 (Table I), which consisted of 13 measurements over a range of HBr concentrations. In order to improve the signal-to-noise, 5000 laser pulses were averaged to obtain each state-selected emission signal. Figure 7 presents a typical set of emission signals from this experiment.

Intensity values, $I(2 \rightarrow 1)$ and $I(1 \rightarrow 0)$, are obtained from these signals and treated according to the discussion in section III.B to obtain the branching ratio, α/β . Branching ratio values determined from peak intensities are obtained by using the experimentally determined time constants in eq 5 and 6. The result from these measurements is $\alpha/\beta = 0.36 \pm 0.04$ (2σ). Selected emission signals were also subjected to a more thorough examination to determine intensity ratios at various points before and after the peak intensities. The branching ratios are in very good agreement except at very long times where the signal intensities are lower. We believe that these measurements provide an accurate value of α/β .

At early times in the rising portion of the signal the approximation, $e^{-k[\text{HBr}]t} \simeq 1 - k[\text{HBr}]t$, is valid. Under this approximation the branching ratio is given simply by eq 12 from the intensity ratio adjusted by the relative detection sensitivity. These intensity ratios at early times ([HBr] $t = (3-6) \times 10^{10}$ molecule cm⁻³ s) yield branching ratio values from 0.40 to 0.47 with an average value of $\alpha/\beta = 0.44 \pm 0.05$ (2σ). Calculations suggest that for $\alpha/\beta = 0.4$ this method underestimates the branching ratio by no more than 10% when [HBr] $t < 9 \times 10^{10}$ molecule cm⁻³ s, even though the approximation is extremely poor for $e^{-k_{\text{RI}}[\text{HBr}]t}$ $\simeq 1 - k_{\text{RI}}[\text{HBr}]t$.

Attempts to obtain α/β from back-extrapolated intensities to t = 0 yielded scattered results that were not useful. We believe that this may be due in part to the long extrapolation required in the $1 \rightarrow 0$ decay, which must be fit only at very long time to remove the τ_{R1} and τ_{V2} components. It is this last (worst) method which was assumed in previous measurements.

The average [HCl(v=2)]/[HCl(v=1)] branching ratio obtained from the intensity ratios by the two methods (26 measurements) is $\alpha/\beta = 0.40 \pm 0.06$ (2σ). This value is supported by the estimate, $\alpha/\beta = 0.34$, from the analysis of the $1 \rightarrow 0$ "rise time" measurements. Excellent agreement is noted with the results of Maylotte et al.¹ (0.4) and Wickramaaratchi and Setser⁴ (0.37), but the values determined by Zwier et al.³ (0.11 ± 0.05) and by Berquist et al.⁴ (0.12) are significantly lower.

We believe that the low value obtained by Zwier et al.³ arises from a combination of two factors:

(1) Ignoring the contribution to the $1 \rightarrow 0$ emission signal from vibrational cascading overestimates the initial population of HCl(v=1) and significantly reduces the value of α/β obtained from the extrapolated intensities at t = 0. An evaluation using eq 7 and 8 for $\alpha/\beta = 0.4$ shows that $[HCl(v=1)]_{vv} \simeq [HCl(v=1)]_0$.

(2) The narrow band dielectric interference filter used in the observations gives a blue shift at incidence angles other than normal.²¹ This effect decreases the relative detection sensitivity of HCl(v=2).

The rate constant for (R1) along with the HCl(v) product state distribution can be used with the principle of microscopic re-

versibility to calculate rate constants for the reverse reactions of Br with HCl(v), which can be compared with experimental determinations.^{5,22-25} The relative population of HCl(v=0) from (R1) is not determined directly in IRCL experiments; however, laser emission observed on the $1 \rightarrow 0$ transition of HCl from (R1) sets the limits, $0 \leq [HCl(v=0)]/[HCl(v=1)] \leq 1$, and [HCl(v=1)]/[HCl(v=0)] is given as 1.5 ± 0.3 by ref 26. Using this value and $\alpha/\beta = 0.4$, we calculate the v=0:v=1:v=2 distribution of HCl(v) from (R1) to be 0.32:0.49:0.19. The detailed rate constant for HCl(v=2) production then is 1.9×10^{-12} cm³ molecule⁻¹ s⁻¹, and the detailed balancing calculation⁵ yields $k(Br+HCl(v=2)) = 5.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This value is two to three times higher than the measured total deactivation rate constants of HCl(v=2) by Br atoms.^{5,22-25} The principle of microscopic reversibility does not give agreement in this system, where k_{R1} , α/β , and k(Br+HCl(v=2)) are all apparently wellknown. This apparent failure may mean that the details of the rotational and translational energy distributions, which have not been considered, may be important in this reaction.

V. Conclusions and Summary

In this work, we have demonstrated the utility of the laserinitiated chemical chain reaction technique in providing accurate rate coefficients for the propagation reactions and vibrational relaxation processes in the Cl_2 + HBr system. We have also demonstrated the need for careful state-selected observations and the application of appropriate multiple state kinetic analyses in determining vibrational state distributions of chemiluminescent products.

The rate coefficients for the chain propagation steps in this system differ by nearly a factor of 10^4 , yet both are accurately obtained from state-selected observations of the HCl(v=2) fluorescence. The value obtained for k_{R1} is ~20-30% higher than has been previously determined from IRCL measurements.⁶⁻⁹ The earlier studies underestimated k_{R1} due to the influence of vibrational cascading on the "rise time" of the combined fluorescence from HCl(v=1) and HCl(v=2). The rate constant for the slow propagation step is obtained from the HCl(v=2) intensity measurements at high [Cl₂]. The previously determined value of k_{R2} is brought into better agreement with the present value when a correction due to vibrational cascading is applied.

This work serves as a warning concerning the insidious behavior of vibrational cascading in IRCL observations. In view of the differences in the temperature dependence of $k_{\rm R1}$ observed by Mei and Moore⁶ and by Rubin and Persky,¹⁰ a reinvestigation of the Cl + HI reaction rate over a range of temperatures would be welcome.

Although k_{V1} measured here agrees well with previous measurements,¹⁵ the only other measurement¹⁸ of k_{V2} is ~40% larger than our value. A v^n dependence has been observed for the deactivation rate constants of other hydrogen halides.^{13,15,27} With only two points, the available data suggest that k_v scales as v^n where $n = 1.2 \pm 0.3$ for the deactivation of HCl(v) by HBr. Measurements of k_v for $v \ge 2$ would be helpful in determining n more accurately. Such measurements would be useful in arriving at an understanding of the reasons for this v^n dependence and the roles played by V–V and V–T,R processes.²⁸

The present investigation should eliminate the confusion concerning the HCl(v=2)/HCl(v=1) branching ratio in (R1); however, the lack of agreement with the principle of microscopic reversibility is not solved. Since the rate constants for both directions of (R1) are now apparently well established and α/β is

(23) Arnold, D.; Wolfrum, J. Ber. Bunsen-Ges. Phys. Chem. 1976, 80, 892.
 (24) Douglas, D. J.; Polanyi, J. C.; Sloan, J. J. J. Chem. Phys. 1973, 59, 6679.

(25) Douglas, D. J.; Polanyi, J. C.; Sloan, J. J. Chem. Phys. 1976, 13, 15.
 (26) Bittenson, S. N. Ph.D. Thesis, University of Wisconsin-Madison, 1977.

⁽²¹⁾ Baker, M. L.; Yen, V. L. Appl. Opt. 1967, 6, 1343.

⁽²²⁾ Leone, S. R.; Macdonald, R. G.; Moore, C. B. J. Chem. Phys. 1975, 63, 4735.

⁽²⁷⁾ Bott, J. F. J. Chem. Phys. 1979, 70, 4123.

⁽²⁸⁾ Coltrin, M. E.; Marcus, R. A. J. Chem. Phys. 1980, 73, 2179. 1980, 73, 4390.

known, more attention should be focused on the rotational and translational energy distributions in attempting to reconcile the detailed balancing calculations.

The present study and other reports^{9,12-14} have shown that simultaneous chemiluminescence observations from multiple vibrational states can lead to errors in the measurements of rate constants and product yields. Some of these errors, while quite subtle, can be large. These results argue strongly for the application of selected single state observations and analyses in IRCL measurements.

Acknowledgment. We gratefully acknowledge the Department of Energy for support of this research program and the National Science Foundation for the laser equipment. D.A.D. thanks the National Bureau of Standards for support through a National Research Council postdoctoral fellowship.

Photocatalytic Activity of TIO_2 Powders Suspended in Aqueous Silver Nitrate Solution. Correlation with pH-Dependent Surface Structures

Bunsho Ohtani,* Yoshitaka Okugawa, Sei-ichi Nishimoto, and Tsutomu Kagiya

Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan (Received: July 18, 1986)

Photocatalytic ($\lambda_{ex} > 300$ nm) activity of anatase and rutile TiO₂ powders suspended in AgNO₃ solution was investigated at room temperature under Ar. The initial rate of the photocatalytic reaction producing O₂ and Ag metal strongly depended upon the pH of suspension, i.e., it decreased with decreasing pH, becoming negligible at pH <2 with anatase and pH <5 with rutile, respectively. The amount of Ag⁺ adsorbed on the TiO₂ surfaces in the dark decreased with decreasing pH from 8 to 2. The pH dependence of TiO₂ activity was attributed predominantly to the Ag⁺ adsorption; the initial rates of the photocatalytic reactions by both anatase and rutile TiO₂ were in proportion to the amount of surface-adsorbed Ag⁺. The characterization of surface hydroxyl groups on the TiO₂ powders by means of potentiometric titration of the aqueous suspensions revealed that decreasing the pH causes the protonation of neutral hydroxyl groups into positively charged ones, which inhibits the Ag⁺ adsorption.

Introduction

A common feature of the photocatalytic reaction by suspended semiconductor powders in aqueous solutions¹ is the remarkable pH dependence of the reaction rate. Such pH-dependent photocatalytic activities of TiO_2/Pt have been demonstrated for dehydrogenation of alcohols,² decomposition of carboxylic acids,³ carbohydrate,⁴ and hydroxylamine,⁵ molecular weight increase or decrease of poly(ethylene oxide),⁶ oxidation of aromatic compounds,⁷ and N-alkylation of amines.⁸ Although the characterization of the pH-dependent photocatalytic action of semiconductor suspensions seems to be quite important, there are few satisfactory studies because of the complexity of photocatalytic systems.

We have previously demonstrated photocatalytic O_2 evolution and Ag metal deposition by metal-unloaded TiO₂ suspended in aqueous silver salt solutions.⁹ In the present work, the pH dependence of reaction rate in this simple photocatalytic system was studied with simultaneous characterization of the amount of adsorbed Ag^+ and hydroxyl groups on the TiO₂ surface. The role of the surface-adsorbed Ag^+ as an electron scavenger in the enhancement of water oxidation is discussed.

Experimental Section

Anatase and rutile TiO₂ powders were supplied from Merck and Wako Pure Chemicals (Osaka, Japan, practical grade), respectively, and used without further activation. The specific surface area of these powders was evaluated from nitrogen adsorption at -196 °C based on the BET equation. The other materials were used as received. Water was passed through ion-exchange resin and distilled before use; the purity was checked by the conductivity of $<0.2 \ \mu\text{S cm}^{-1}$.

The finely ground TiO₂ powder (250 mg) was suspended in 2.00 $\times 10^{-3}$ -1.00 $\times 10^{-2}$ mol dm⁻³ AgNO₃ aqueous solution (5.0 cm³, containing 9 $\times 10^{-2}$ mol dm⁻³ KNO₃) in a glass tube (18 mm in diameter and 180 mm in length, transparent for the light of wavelength >300 nm). The pH of the suspension was adjusted by adding 1.00×10^{-1} mol dm⁻³ NaOH or HNO₃ (<0.15 cm³). The suspension was sonicated for 5 min, purged with Ar for >30 min, and then sealed off with a rubber stopper. Irradiation was performed with a 400-W high-pressure mercury arc at 27 ± 2 °C. The TiO₂ suspension was magnetically stirred throughout the irradiation. Product analyses were performed as described elsewhere.⁹ Quantum efficiency was conveniently estimated by using a Blak-Ray J-221 ultraviolet meter on the assumption that the incident light consists of photons at 365 nm.

The amount of Ag^+ adsorbed on the TiO_2 surface in the dark, under conditions similar to the photocatalytic reaction, was de-

⁽¹⁾ For a review see: Bard, A. J. J. Phys. Chem. 1982, 86, 172.

^{(2) (}a) Kawai, T.; Sakata, T. Chem. Lett. 1981, 81. (b) Nishimoto, S.;
Ohtani, B.; Sakamoto, A.; Kagiya, T. Nippon Kagaku Kaishi 1984, 246. (c) Nishimoto, S.; Ohtani, B.; Shirai, H.; Kagiya, T. J. Polym. Sci., Polym. Lett. Ed. 1985, 23, 141. (d) Nishimoto, S.; Ohtani, B.; Kagiya, T. J. Chem. Soc., Faraday Trans. 1 1985, 81, 2467. (e) Nishimoto, S.; Ohtani, B.; Shirai, H.; Kagiya, T. J. Chem. Soc., Perkin Trans. 2 1986, 661.

Kagiya, T. J. Chem. Soc., Perkin Trans. 2 1986, 661.
 (3) (a) Kraeutler, B.; Bard, A. J. J. Am. Chem. Soc. 1978, 100, 5985. (b)
 Yoneyama, H.; Takao, Y.; Tamura, H.; Bard, A. J. J. Phys. Chem. 1983, 87, 1417. (c) Sakata, T.; Kawai, T.; Hashimoto, K. J. Phys. Chem. 1984, 88, 2344.

⁽⁴⁾ St. John, M. R.; Furgala, A. J.; Sammells, A. F. J. Phys. Chem. 1983, 87, 801.

⁽⁵⁾ Oosawa, Y. J. Phys. Chem. 1984, 88, 3069.

⁽⁶⁾ Nishimoto, S.; Ohtani, B.; Shirai, H.; Adzuma, S.; Kagiya, T. Polym. Commun. 1985, 26, 292.

⁽⁷⁾ Fujihira, M.; Satoh, Y.; Osa, T. Bull. Chem. Soc. Jpn. 1982, 55, 666.
(8) Nishimoto, S.; Ohtani, B.; Yoshikawa, T.; Kagiya, T. J. Am. Chem. Soc. 1983, 105, 7180.

⁽⁹⁾ Nishimoto, S.; Ohtani, B.; Kajiwara, H.; Kagiya, T. J. Chem. Soc., Faraday Trans. 1 1983, 79, 2685.