Laser-Initiated Chemical Chain Reactions: Termination Kinetics of the Cl_2/HBr/NO Chain System

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The termination steps of the laser-initiated Cl_2/HBr chemical chain reaction have been studied via time-resolved infrared chemiluminescence (IRCL) from the vibrationally excited HCl(v) product molecules. Laser photolysis/IRCL experiments were conducted at 298 ± 3 K in slowly flowing gas mixtures of Cl_2, HBr, and NO diluted in Ar. The termolecular association of Br* with NO (M = Ar) competed with the second propagation step for the Br* chain carrier, thereby terminating the chain. The resulting pseudo-first-order decay rates of the steady-state IRCL signal were obtained with 6–60 Torr of argon as the third-body collision partner. The low-pressure rate coefficient for Br* + NO + Ar → BrNO + Ar was determined to be $k_3 = 8^{+3}_{-4} \times 10^{-32}$ cm^6 molecule^{-2} s^{-1} at 298 K. The present work demonstrates the utility of the laser-initiation/IRCL method in kinetic measurements of chain termination rates. This technique may be applicable as a competitive method for measuring rate coefficients for other radicals that can be incorporated into a chain reaction via H atom abstraction.

I. Introduction

In recent years, infrared chemiluminescence (IRCL) detection has been used in kinetic studies of laser-initiated chemical chain reactions characterized by the following scheme:[1-7]

$$X_2 + h\nu \rightarrow 2X^\bullet \qquad \text{(laser initiation)}$$

$$X^\bullet + RH \xrightarrow{k_1} HX(v) + R^\bullet \qquad \text{(chain propagation)}$$

$$R^\bullet + X_2 \xrightarrow{k_2} RX + X^\bullet \qquad \text{(chain propagation)}$$

$$HX(v) + RH \xrightarrow{k_v} HX + RH \qquad \text{(vibrational relaxation)}$$

where X* = halogen and R* = an atom or small radical. Reaction rates were determined in these studies by time-resolved detection of infrared fluorescence from the vibrationally excited HX(v) product. These studies were an outgrowth of investigations of hydrogen halide chemical laser reactions. Braithwaite and Leone[1] first detected chain behavior in an IRCL study of the laser-initiated Cl* + H_2S reaction. Nesbitt and Leone[2-5] subsequently developed a formal analysis of the pseudo-first-order chain kinetics and reported investigations of a number of Cl_2/RH chain systems, where RH = H_2S, CH_3SH, H_2, HBr, and several hydrocarbons. Dolson and Leone,[6,7] in investigations of the Cl_2/HI, Br_2/HI, and Cl_2/HBr chain systems, extended the analysis to include the effects of vibrational cascading and demonstrated that vibrationally state selected observations were necessary for accurate chain propagation rate measurements.

The current work[8] extends the IRCL method to include a systematic study of the termination kinetics of laser-initiated chemical chain reactions. This extension of the technique was conceived initially as a competitive method for measuring reaction rates of the radical chain carrier, R*, with an added reactant. It was suggested by a consideration of the following information: (i) A significant characteristic of the IRCL observations in the laser-initiated chemical chain reactions is the generation of a steady-state intensity on the time scale beyond that of vibrational relaxation.[2,3,5-7] (ii) The removal of chain carrier, R*, by a competitive reaction would result in chain termination, evidenced by decay of the steady-state IRCL signal level. (iii) This exponential decay of the steady-state signal would provide a general means of measuring the rates of such competing reactions.

A demonstration of this concept and its utility in obtaining kinetic rate coefficients is presented here. In this demonstration the competing reaction is brought about by the addition of a radical scavenger, NO, to the linear Cl_2/HBr chain reaction. This chain system was chosen for the demonstration because the nonterminating chain has been extensively characterized by the IRCL technique.[3,5,7] The general chain reaction scheme is modified by the addition of a scavenger such as NO:

$$X^\bullet + RH \xrightarrow{k'_1} R^\bullet + HX(v) \qquad (1)$$

$$R^\bullet + X_2 \xrightarrow{k'_2} RX + X^\bullet \qquad (2)$$

$$R^\bullet + NO + M \xrightarrow{k'_3} RNO + M \qquad (3)$$

$$X^\bullet + NO + M \xrightarrow{k'_4} XNO + M \qquad (4)$$

$$HX(v) + RH \xrightarrow{k'_{v,RH}} HX + RH \qquad (5)$$

$$HX(v) + NO \xrightarrow{k'_{v,NO}} HX + NO \qquad (6)$$

The primes are used here to denote the true rate coefficients. Later, the pseudo-first-order rate coefficients will be written without the prime. The competing termination reaction (3) is termolecular, although competing first- or second-order reactions would terminate the chain similarly. The radical scavenger competes with *both* propagation steps for the chain carries, so that reaction 4 also must be included in the reaction scheme. We will show later that the effect of reaction 4 is observed in the signal rise. Thus, the measurement of k'_3 from the steady-state decay is not obscured by the companion termination reaction (4). Similar termolecular termination reactions have been proposed as the source of the inhibitive effect of O_2 on the Cl_2/H_2 chain system.[9,10]

The experiments described here are similar in spirit to experiments reported by Fasano and Nogar[11] and by Smith and Wrigley.[12] Using the IRCL technique and a simpler (non-chain)

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reaction, $F^{\bullet} + H_2 \rightarrow HF(v) + H^{\bullet}$, Fasano and Nogar[11] measured the rate coefficient for the competing three-body reaction, $F^{\bullet} + NO_2 + M \rightarrow FNO_2 + M$, from signal rise times. Earlier, Smith and Wrigley[12] similarly obtained the rate coefficient for $F^{\bullet} + O_2 + M \rightarrow {}^{\bullet}FO_2 + M$ in competition with $F^{\bullet} + HX \rightarrow HF(v) + X^{\bullet}$ (X = Cl, Br). Their success suggests that the IRCL technique should be applicable in the study of three-body termination steps of chain reactions.

We present a pseudo-first-order kinetic solution for reactions 1–6, the general X_2/RH chain system terminated by NO. The rate coefficient for reaction 3, $Br^{\bullet} + NO + Ar \rightarrow BrNO + Ar$, is reported and compared to the value reported for helium as the third-body collision partner. The success of this work demonstrates the effectiveness of the IRCL method in obtaining termination rate coefficients in laser-initiated chemical chain reactions. In principle, it should be possible to study other reactions of various radical species, $R^{\bullet}$, by the competitive termination of a chain reaction. This may prove to be a valuable technique in cases where sensitive, selective detection methods for $R^{\bullet}$ do not exist. We intend to investigate this potential further in a future work.

II. Kinetic Analysis of the Terminated Chain System

With the addition of a radical scavenger, NO in the present case, the kinetic scheme involves reactions 1–6. The following psuedo-first-order rate coefficients will be used for the development of the differential equations:

$$k_1 = k'_1[RH] \tag{7}$$

$$k_2 = k'_2[X_2] \tag{8}$$

$$k_3 = k'_3[NO][M] \tag{9}$$

$$k_4 = k'_4[NO][M] \tag{10}$$

The differential equations for the chain carriers in the terminated chain system are

$$d[X^{\bullet}]/dt = -(k_1 + k_4)[X^{\bullet}] + k_2[R^{\bullet}] \tag{11}$$

$$d[R^{\bullet}]/dt = k_1[X^{\bullet}] - (k_2 + k_3)[R^{\bullet}] \tag{12}$$

The specific solutions[8] for these differential equations are

$$[X^{\bullet}]/[X^{\bullet}]_0 = A \exp(\lambda_- t) + (1 - A) \exp(\lambda_+ t) \tag{13}$$

$$[R^{\bullet}]/[X^{\bullet}]_0 = B[\exp(\lambda_+ t) - \exp(\lambda_- t)] \tag{14}$$

where $A \approx B \approx k_1/(k_1 + k_2)$ are valid approximations for the conditions of this study, and where λ_+ and λ_- are given by

$$\lambda_{\pm} = \{-(k_1 + k_2 + k_3 + k_4) \pm [(k_1 + k_2 + k_3 + k_4)^2 - 4(k_1k_3 + k_2k_4 + k_3k_4)]^{1/2}\}/2 \tag{15}$$

Note that the $\lambda_{\pm}$ are *negative* quantities and that the time-dependent concentrations vary with observed rates, $-\lambda_+$ and $-\lambda_-$, of which $-\lambda_-$ is the faster rate. The $\lambda_{\pm}$ expressions simplify to $\lambda_+ \approx -k_3$ and $\lambda_- \approx -(k_1 + k_2 + k_4)$ with a high degree of accuracy for the condition, $k_1 \gg k_2$. The mathematical details of this simplification and limits of the approximations have been developed elsewhere.[8] Equations 13 and 14 indicate that the photolytically generated halogen atom concentration in the terminated chain system undergoes a double-exponential decay while the radical produced in the second propagation step rises exponentially and then slowly decays. Under the reaction conditions of this study, $k_1 \geq 250\,k_2$, so that $k_3 = -\lambda_+$ was a valid approximation.

The slow decay is confirmed to be k_3 also by a simple consideration of the loss rate of chain carriers, given by the sum of eqs 11 and 12:

$$d([X^{\bullet}] + [R^{\bullet}])/dt = k_4[X^{\bullet}]_{ss} + k_3[R^{\bullet}]_{ss} \tag{16}$$

where the steady-state concentrations of the chain carriers are[2,5]

$$[X^{\bullet}]_{ss}/[X^{\bullet}]_0 = k_2/(k_1 + k_2)$$

$$[R^{\bullet}]_{ss}/[X^{\bullet}]_0 = k_1/(k_1 + k_2) \tag{17}$$

Because of the magnitudes of k_1 and k_2, eq 16 is accurately approximated by its second term alone. Thus, k_3 is shown to be the termination rate for the chain carriers.

The vibrationally excited $HX(v)$ product is observed in the IRCL experiments. Consequently, an algebraic expression for $[HX(v)]$ is of the greatest importance for this work. The normalized expression for the highest $HX(v)$ vibrational level produced in (1) is

$$[HX(v)]/[X^{\bullet}]_0 = C \exp(\lambda_+ t) - D \exp(\lambda_- t) + (D - C) \exp(-k_v t) \tag{18}$$

where k_v is the collisional relaxation rate, $k_v = k'_{v,RH}[RH] + k'_{v,NO}[NO]$, and the coefficients are given in ref 8. The $HX(v)$ IRCL signal for the terminated chain is predicted to rise with rate, $-\lambda_-$, undergo a fast decay with rate, k_v, and then slowly decay with rate, $-\lambda_+ \approx k_3$. Thus, we may obtain the pseudo-first-order chain termination rate, k_3, *directly* from the slow decay of the IRCL signal.

III. Experimental Methods

The experimental apparatus used in this work was similar to those used in previous laser-initiated chain reaction studies.[1-7] It consisted of a halocarbon wax-coated flow cell in which the reagent gases were diluted in a flow of argon and irradiated with the 355-nm output of a Q-switched Nd:YAG laser (8 ns, ≤4 mJ, 20-mm expanded beam diameter) to initiate the reaction scheme. The spontaneous infrared fluorescence near 3.5 μm from the $HCl(v)$ reaction product was spectrally filtered for observation a specific vibrational state and detected with a fast infrared detector. The amplified detector signal was signal averaged with a digital oscilloscope. The signal vs time data were fitted to the appropriate $[HCl(v)]$ expressions using a nonlinear least-squares procedure available in a commercially available MS-DOS software package.[13]

Reagent gas distillation and storage was achieved with a conventional glass vacuum line having a background pressure of $<10^{-5}$ Torr. Cl_2, semiconductor grade (99.99%), was used without further purification. HBr(99+%) was distilled from 156 K (ethanol slush) to 77 K on the vaccum line keeping only the middle fraction, which was stored in 12-L glass bulbs attached to the vacuum line. Argon (99.999%) was passed through a molecular sieve trap directly upstream of the flow controller. NO (99.0%) was passed over glass beads in a 50 cm^3 stainless steel cylinder, which was placed upstream of the flow controller and cooled to 156 K with an ethanol slush.[14]

Pressure measurements in the photolysis cell were made via 10, 100, or 1000 Torr capacitance manometers (0.15% rated accuracy) attached directly to the cell. The volume flow rates of the gases were maintained by electronic flow controllers. Laboratory calibrations of flow rates were made frequently. Concentrations were calculated from the total gas pressure and the flow rates of the gases.

A 77 K HgCdTe semiconductor detector (16 mm^2 active area, 0.2-μs rise time) and an interference filter having a central wavelength of 3.47 μm (fwhm = 0.2 μm) were used to detect

emission from HCl(v=1), with a smaller contribution from HCl(v=2). Each digital waveform, consisting of 2500 points, was averaged for 1000 laser shots.

IV. Results and Discussion

The rate coefficients for the propagation steps and vibrational deactivation of the HCl(v) product of the Cl_2/HBr chain system are readily available in literature. The first propagation step, $Cl^\bullet + HBr \rightarrow HCl(v) + Br^\bullet$, is exothermic by 65.0 kJ/mol,[15] and the HCl(v=2)/HCl(v=1) product ratio is 0.40 ± 0.06.[7] Dolson and Leone[7] reported $k'_1 = (1.02 \pm 0.15) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, in agreement with the relative rate measurement of Rubin and Persky,[16] and presented an explanation for the lower results from earlier studies[3,5,17-19] using the IRCL technique.

Two experimental studies have found lower k' values. Lamb et al.[20] used the very low pressure reactor technique to determine $k'_1 = 3.4 \times 10^{-12}$ cm^3 molecules^{-1} s^{-1}. Nicovich and Wine[21] monitored the decay of [Cl$^\bullet$] via resonance fluorescence (RF) following laser photolysis of Cl_2. They reported $k'_1 = (5.6 \pm 0.6) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and suggest that k'_1 of Lamb et al.[20] may be low due to a probable reverse reaction; however, no explanation is evident for the difference between the IRCL results and their RF result.

The second propagation step, $Cl_2 + Br^\bullet \rightarrow BrCl + Cl^\bullet$, is endothermic by 24.1 kJ/mol.[15] Nesbitt and Leone[3] obtained the rate coefficient, $k'_2 = (2.4 \pm 0.2) \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}, in agreement with the value calculated from the principle of detailed balancing and the rate coefficient for the reverse reaction.[22] Dolson and Leone[7] remeasured k'_2 observing *only* v = 2, which should lead to a more accurate value for k'_2, and obtained a value of (1.1 ± 0.4) × 10^{-15} cm^3 molecule^{-1} s^{-1}.

Rate coefficients for vibrational deactivation of HCl(v=2) by HBr have been reported by Dasch and Moore[23] as (2.9 ± 0.3) × 10^{-12} cm^3 molecule^{-1} s^{-1} and by Dolson and Leone[7] as (2.09 ± 0.50) × 10^{-12} cm^3 molecule^{-1} s^{-1}. There is general agreement[24] that the vibrational deactivation rate coefficient for HCl(v=1) by HBr is 1.1 × 10^{-12} cm^3 molecule^{-1} s^{-1}.

The rate coefficients for the unterminated chain system were remeasured in the early part of this work to ensure the validity of the IRCL technique employed in our laboratory.[8] These verification experiments reproduced the k'_1 values of refs 7 and 16 quite well. Vibrational deactivation rate coefficients were also in good agreement with the literature values quoted above. The measurement of k'_2 was accomplished from a ratio of intensities[3,7] and was found to be sensitive to the manner in which the steady-state intensity was obtained from the data. This was due to poor steady-state signal-to-noise (S/N) ratios resulting from the use of two "cold" gas filters, as described previously,[7] to isolate HCl(v=2) emission.

k'_3 Measurement. k'_3 measurements were obtained from HCl(v=1) observations, which could be made with higher S/N ratios than HCl(v=2) observations. In addition to the direct production of HCl(v=1) in reaction 1, HCl(v=1) is also produced by the V–V relaxation of HCl(v=2). This results in the addition of a *fourth* exponential term to the mathematical description of [HCl(v=1)]:

$$[HCl(v=1)]/[X^\bullet]_0 = A\exp(\lambda_- t) + B\exp(\lambda_+ t) + C\exp(-k_{v=2}t) + D\exp(-k_{v=1}t) \quad (19)$$

where $k_{v=2}$ is the rate of HCl(v=2) deactivation, $k_{v=1}$ is the rate of HCl(v=1) deactivation, and the coefficients are given elsewhere.[8] According to eq 19 the IRCL signals should appear as two exponential rises followed by two decays. Since the slow (λ_+) decay occurs on a much longer time scale than the collisional relaxation of HCl(v), the HCl(v=1) emission should provide an uncomplicated view of the slow decay. Furthermore, the vibrational cascading from HCl(v=2) into HCl(v=1) gives more relative intensity to the slower (λ_+) decay of the HCl(v=1) emission than would be found for the λ_+ decay of the HCl(v=2) emission.[6]

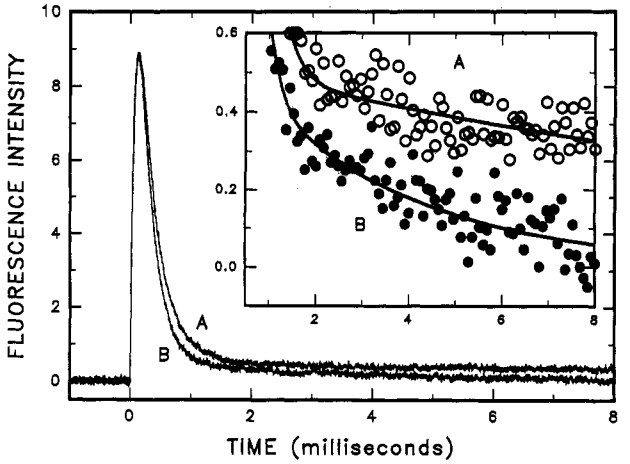

Figure 1. Influence of NO upon the slow decay rate of HCl(v=1) in the Cl_2/HBr chain reaction. The HBr, Cl_2, and Ar pressures were 0.067, 2.19, and 30.0 Torr, respectively. The NO pressure was 0.016 Torr in trace A (open circles) and 0.111 Torr in trace B (closed circles). The inset box shows an expanded view of the slow decays and their double exponential decay fits. The data point density has been reduced by a factor of 20 in the expanded box for clarity.

Six sets of experiments were conducted to determine k'_3 at argon concentrations over the range (0.20–2.0) × 10^{18} molecules cm^{-3}. In each set of experiments, [Cl_2] and [HBr] were held constant as [NO] was varied to increase the chain termination rate. Each set of experiments consisted of observations of HCl(v=1) emission at five or six values of [NO]. [Cl_2] and [HBr] values were (5.7–8.8) × 10^{16} molecules cm^{-3} and (1.4–3.4) × 10^{15} molecules cm^{-3}, respectively, in the six sets of experiments. The relatively high [Cl_2] values were necessary to "drive" the slower second propagation step and generate an observable steady-state HCl(v) intensity. The 355-nm laser was operated at 4 mJ/pulse at 5 Hz, and 1000 laser shots were averaged for each observation. The ratio [HBr]/[Cl$^\bullet$]$_0$ ranged from 22 to 35 for all of these experiments, ensuring a high degree of pseudo-first-order behavior.

Figure 1 presents two HCl(v=1) observations at different [NO] values, obtained with the narrow-bandwidth interference filter. The more noticeable effects of increasing [NO] are the increased decay rates. The expanded intensity scale of the inset box gives a better view of the slow decay. Data of this type were fitted to a double exponential decay function for times judged to be beyond the influence of the HCl(v=2) relaxation, $t > 5/k_{v=2}$. These times were calculated from experimental concentrations using $k'_{v=2,HBr} = 2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and $k'_{v=2,NO} = 2.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.[25] Limited attempts to fit the entire observation beyond t = 0 to a sum of four exponential terms (eq 19) were unsatisfactory. The rates for deactivation of HCl(v=1) and HCl(v=2) differ only by a factor of 2. Consequently, the fitting algorithm could not distinguish more than three distinct time constants. These efforts did, however, provide slow decay rates for comparison with the values from the double exponential fits. The absolute agreement was better than ±20 s^{-1} for the slow decay rates of the two observations in Figure 1.

We have shown that these slow decay rates may be taken to be $k_3 = k'_3[Ar][NO]$. The plots of k_3 versus [NO] for six argon pressures, presented in Figure 2, yielded values of k'_3[Ar] from the slopes of linear fits of the data. A summary of data for the k'_3 determination is presented in Table I. A plot of the k'_3[Ar] values versus [Ar] for the six sets of experiments is presented in Figure 3. The value obtained for k'_3 from the slope of Figure 3 was 8.3 × 10^{-32} cm^6 molecule^{-2} s^{-1}.

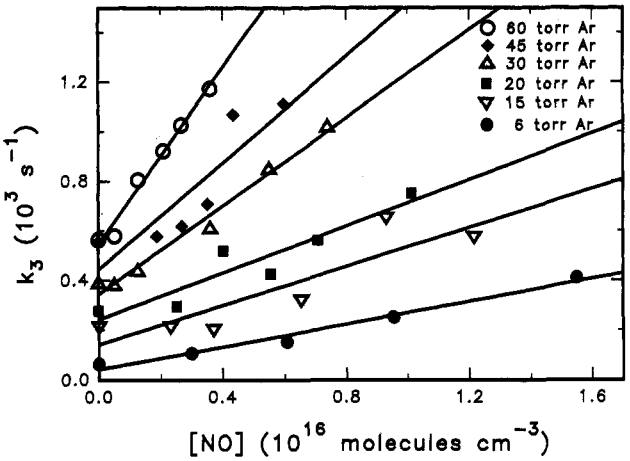

Figure 2. Rate of HCl(v=1) slow decay as a function of nitric oxide and argon concentrations. The solid lines are linear fits to the data. The slopes of these lines are the k'_3[Ar] values listed in Table I and plotted in Figure 3. The data have been adjusted vertically for clarity.

TABLE I: HCl(v=1) Show Decay Results for k'_3 Determination[a]

[Cl_2]	[HBr]	[Ar]	[NO]	k'_3[Ar][b]	k'_3[c]
5.73(16)	1.39(15)	2.01(17)	0–1.62(16)	2.27(–14)	11.3(–32)
7.55(16)	2.92(15)	4.41(17)	0–1.22(16)	3.91(–14)	8.9(–32)
8.20(16)	3.15(15)	6.27(17)	0–1.01(16)	4.70(–14)	7.5(–32)
7.10(16)	2.17(15)	9.69(17)	0–7.39(15)	8.91(–14)	9.2(–32)
8.80(16)	3.38(15)	1.46(18)	0–5.99(15)	1.10(–13)	7.5(–32)
7.13(16)	2.17(15)	2.00(18)	0–3.60(15)	1.78(–13)	8.9(–32)

[a] Concentrations are given in units of molecules cm^{-3}, with exponents of 10 in parentheses. [b] k'_3[Ar] values, in units of cm^3 $molecule^{-1}$ s^{-1}, are the slopes from Figure 2. [c] cm^6 $molecule^{-2}$ s^{-1}.

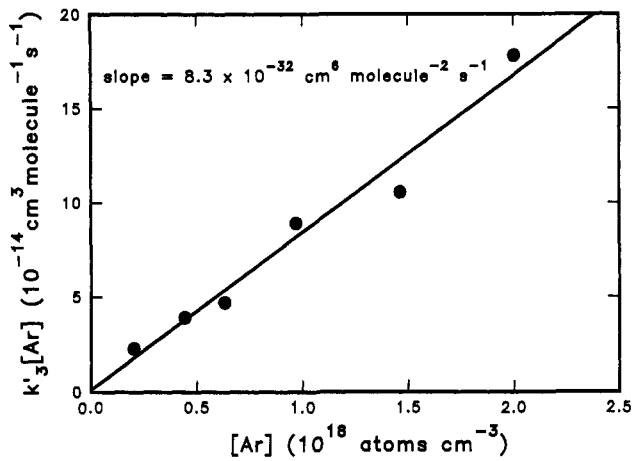

Figure 3. Pseudo-second-order rate coefficient, k'_3[Ar], as a function of argon concentration. The slope of the linear fit is the low-pressure termolecular rate coefficient for Br• + NO + Ar → BrNO + Ar, k'_3 = 8.3 × 10^{-32} cm^6 $molecule^{-2}$ s^{-1}.

We considered the contribution of second-order losses of Br• to the slow decay because of the necessity of operating with elevated [Cl•]$_0$. After a few chain cycles, the steady-state bromine atom concentration approaches that of the initial chlorine atom concentration, [Br•]$_{ss}$ ≅ [Cl•]$_0$. The initial rate of Br• recombination can be calculated using k'_{rec} = 6.6 × 10^{-33} cm^6 $molecule^{-2}$ s^{-1}.[26] The initial recombination rate for 3 mTorr Br• atoms in 60 Torr Ar is k'_{rec}[Br•]$_{ss}$[Ar] = 1.2 s^{-1}, which is less than 2% of the Br• loss rate of reaction 2. Since this recombination is not dependent upon [NO] it should not affect the k'_3 determination.

The bimolecular reaction

$$Br^\bullet + BrNO \rightarrow Br_2 + NO \qquad (20)$$

was also a concern at high [Cl•]$_0$. The rate coefficient for this reaction is 2.2 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}.[27] Calculations of [Br•] versus time were made for 30 Torr of Ar using the GEAR program[28] and a kinetic scheme involving reactions (1–3 and 20) and Br• recombination. We used literature values for k'_1,[7] k'_2,[7] k'_{rec},[26] and k'_{20},[27] and k'_3 = 8.3 × 10^{-32} cm^6 $molecule^{-2}$ s^{-1}. Initial reactant pressures for this calculation were 2.2 Torr of Cl_2, 0.07 Torr of HBr, 0.0024 Torr of Cl•. Calculations were made for 0.1 and 0.2 Torr of NO with *and* without reaction 20. A simple exponential decay analysis provided an adequate fit of the [Br•] versus time data. A comparison of the first-order decay rates indicated that the contribution of reaction 20 increased the slow decay rate by only ~10% at 30 Torr of Ar. We estimate ±30% (2σ) overall uncertainty for our measurement of k'_3 and report $k'_3 = 8^{+3}_{-4} \times 10^{-32}$ cm^6 $molecule^{-2}$ s^{-1}. The negative uncertainty was enlarged to allow for the effect of reaction 20.

The only other measurement of k'_3 with which we can compare our values was made with M = He by Hippler et al,[29] who obtained k'_3(M=He) = (9.4 ± 3.6) × 10^{-33} cm^6 $molecule^{-2}$ s^{-1} over the range 1–100 atm of helium. Using k(He)/k(Ar) = 0.6, as they suggest, would make their rate coefficient k'_3(M=Ar) = (1.6 ± 0.6) × 10^{-32} cm^6 $molecule^{-2}$ s^{-1}, which is still significantly lower than our value. Troe[30] has calculated the strong-collision association rate coefficient for (3) to be k^{sc} = 9.6 × 10^{-32} cm^6 $molecule^{-2}$ s^{-1} at 300 K. Using the collision efficiency determined for M = Ar in the I + NO + Ar association reaction, β_c = 0.45,[31] we calculate k'_3(M=Ar) = 4.3 × 10^{-32} cm^6 $molecule^{-2}$ s^{-1}. This prediction is more than 2.5 times greater than the previous experimental measurement[29] and nearly a factor of 2 lower than the experimental value from the present study.

The experimental methods and pressure region used by Hippler et al.[29] to obtain k'_3 are quite different from the present study. Neither method directly observes the Br• reactant or the BrNO product of reaction 3. Hippler et al.[29] observed the re-formation of Br_2 from reaction 3 followed by (20), while we observe HCl(v) in order to detect the competition between reactions 3 and 2. Relying upon their indirectly measured k'_{20} = (3.8 ± 1.7) × 10^{-10} cm^3 $molecule^{-1}$ s^{-1}, the data analysis of the earlier study[29] required a more elaborate numerical treatment than was involved in the analysis of the IRCL observations in our study. Price and Ratajczak,[27] with a more direct pseudo-first-order measurement, reported a much lower k'_{20} = (2.2 ± 0.7) × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}. This smaller value for k'_{20} is qualitatively consistent with an increase in the k'_3 value of Hippler et al.[29]

The potential for flashlamp generation of Br•*($^2P_{1/2}$) and its impact upon the kinetic observations were not addressed in the previous study.[29] A comparison of the Br_2 absorption spectrum[32] and the subsequent Br* quantum yield measurements[33] suggets the need for such a consideration.[34] Relaxation of Br•* to the $^2P_{3/2}$ ground state in 0.3 torr Br_2 and 0.12 torr NO has a calculated $1/e$ lifetime of ~63 μs,[35] which would appear to overlap significantly with the time scale of the Br_2 reformation observations. The smaller k'_{20} value of Price and Ratajczak[27] would predict a larger steady-state BrNO population than was considered by Hippler et al.,[29] so that Br•* + BrNO collisions might have been important. Sedlacek and Wight[36] have determined that the rate coefficient for Br•* deactivation by BrNO is (1.5 ± 0.2) × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} and that "reactive quenching to form Br_2 + NO is probably a minor channel".

Evaluation of the Technique. The technique used in this study is an extension of the laser photolysis–IRCL method. As such, it has many of the same advantages of the parent technique. Laser photolysis allows for selective photolysis of the desired precursor and control of [X•]$_0$ over several orders of magnitude by adjustments of [X_2] and laser fluence. The entire time evolution of the signal is obtained with each photolysis laser pulse. The IRCL method does not require a second laser or other light source to probe time-dependent concentrations. Any radical, R•, that can be generated by H atom abstraction can, in principle, be studied by this technique. The kinetic rates are always obtained

from sensitive real-time observations of HX(v). Thus, the success of the technique requires that HX(v) be produced in the abstraction reaction, X• + RH → HX(v) + R•, and that R• regenerates X• in a second propagation step. While chain propagation is a requirement, this competitive method can be used even when the chain length is low, as was the case in the current demonstration. The range of k_1 ((1.5–3.5) × 10^4 s^{-1}) and k_2 (60–100 s^{-1}) values used in this study generated typical (unterminated) HCl chain lengths[8] of only 1.1 at 2 ms to 1.8 at 8 ms. By comparison, the maximum k_3 values were ~600 s^{-1}.

Whereas the selective observation of the highest HX(v) vibrational state is necessary for accurate propagation rate measurements,[7] this is *not* true for the slow decay rate measurements demonstrated here. Since the time scale for the slow decay is beyond the collisional relaxation times, all vibrational levels will exhibit the same slow decay rate. Consequently, vibrationally state-selected observations are not required for the slow decay rate measurements. In fact, the inclusion of the lower HX(v) levels in the observations increases the relative intensity of the slow decay.[6]

We measured k'_3 at argon pressures of 6–60 Torr in the evaluation experiments described here. The experimental pressure range may be extended above 1 atm for termolecular reactions if argon or helium is used as the third body, M, because argon and helium are inefficient in relaxing HX(v).[24] The relative steady-state intensity of a specific HX(v) state scales as k_2/k_v, so that the intensity is diminished for efficient collisional relaxation partners.

When experimental control forces $k_1 \gg k_2, k_3$ may be obtained *directly* from the slow decay rate of the HX(v) signal. Signal levels may become too low to run experiments if [X_2] cannot be made small enough to force $k_1 \gg k_2$. In such a case, k_3 could be obtained from the sum, $-(k_1 + k_2 + k_4 + \lambda_- + \lambda_+) = k_3$; however, the magnitude of k_3 may be of the same order of magnitude as the uncertainty in the sum.[8] Many X• + RH reactions are sufficiently rapid, so this situation is likely to be rare.

V. Summary and Conclusions

The laser initiation/IRCL technique has been extended in the current work to the investigation of termination kinetics in halogen + RH chemical chain reactions. The Cl_2/HBr chain system, terminated with NO, was chosen for evaluation of the technique. Algebraic expressions were developed for the time-dependent concentrations of chain carriers, propagation products, and termination products[8] under pseudo-first-order conditions. The concentration of vibrationally excited HX(v), the species detected in this technique, was predicted to exhibit a pseudo-first-order slow decay rate which, for the conditions of this study, were accurately approximated as the chain termination rate. The rate coefficient for Br• + NO + Ar → BrNO + Ar was obtained from experimental measurements of the slow decay rate as a function of NO and Ar concentrations. Secondary losses of the chain carriers were shown to have only a small contribution to the experimental observations. The results presented here demonstrate the ability of the laser initiation/IRCL technique to obtain chain termination rates. The technique worked well, even for the low steady-state intensity (<10% of the peak intensity) encountered in the Cl_2/HBr chain reaction system.

This technique is expected to be useful as a competitive method for measuring rate coefficients for radicals that may be incorporated into a chain reaction via H atom abstraction from suitable precursors. Since the technique always observes HX(v), it may prove to be particularly useful when direct detection of R• is difficult. We anticipate that the technique will be particularly applicable to the evaluation of industrially important laser-initiated chemical chain reactions and to termolecular reactions of atmospheric interest.

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