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Laser initiated chain reactions: A generalized extension to complex chemical chain systems

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We present a generalized extension of the detailed kinetic and experimental analysis for studying rapid gas phase chemical chain reactions initiated by short pulse laser photolysis. The key ingredients of the technique are pulsed laser initiation of the chain by dissociation of a small fraction of a precursor molecule to produce radicals ($Cl_2 \xrightarrow{k_{\perp}} Cl + Cl$), followed by time resolved, infrared chemiluminescence detection of product HCl(v)emission from the propagation steps ($Cl + RH \xrightarrow{k_1} R + HCl(v)$, $R + Cl_2 \xrightarrow{k_1} Cl + RCl$). This laser initiated chain reaction technique is now extended to encompass a far wider range of chain kinetic rates, mechanisms, and product state distributions. Three prototypical systems are investigated which demonstrate distinctly different facets of the extended technique: (1) Cl_2/HBr —a slow chain reaction system, (2) Cl_2/CH_3SH —a multiple chain reaction system, and (3) Cl_2/H_2 —a slow starting chain reaction system in which the product emission appears after an initial induction period. Quantitative rate data are obtained for several chain propagation steps: $Br + Cl_2 \rightarrow Cl + BrCl$, $k = 2.4(\pm 0.2) \times 10^{-15}$ cm³ molecule⁻¹ s⁻¹;

 $Cl + CH_3SH \rightarrow CH_2SH + HCl(v), k = 4.3(\pm 1) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}; CH_2SH + Cl_2 \rightarrow Cl + ClCH_2SH, k = 2.6(\pm 1) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The results illuminate a more general approach to precise kinetic and mechanistic studies of complex chain reactions under nearly ideal psuedo-first-order laboratory conditions.

I. INTRODUCTION

Chemical chain reaction phenomena form the fundamental mechanistic unit of complex combustion systems. As a consequence, a tremendous effort has been directed toward a detailed understanding of chemical chain processes in the past 60 years. Early methods of chain reaction investigation involved observing combustible gas mixtures for onset of explosive behavior under varied conditions of temperature, pressure, and radical scavenger concentration. 1-3 Explosion limits and product analysis can then be used to infer the correct initiation, propagation, and termination mechanisms. Unfortunately, these results tend to be sensitive to the physical environment of the chain reaction, i.e., wall materials,⁴ diffusion effects,⁵ etc., rather than to the intrinsic chain chemistry. With the advancing technology of radical generation and detection, alternatives for quantitative chain studies are available. The individual steps postulated from bulk gas studies can be investigated by generating the desired radical species directly and monitoring the subsequent reactions. 6-8 A wealth of information on isolated radical reactions has been produced by flow tube studies^{9,10} and time resolved photolysis experiments.¹¹⁻¹⁴ Similar progress has been made in the field of ion-molecule kinetics.¹⁵ More recently, laser induced fluorescence techniques¹⁶ have revolutionized product state detection of selected radical reactions; detection limits of 10⁵ molecules cm⁻³ have been reported.¹⁷

Combustion research has traditionally focused on one of two complementary extremes: bulk studies of combustible gas mixtures and studies of isolated radical reactions, both of which have received considerable experimental attention. It is towards a further understanding of the middle ground of combustion research, the study of complex gas phase chain reaction phenomena under simplified experimental conditions, that this paper is directed.

In an earlier work, ¹⁸ we presented a detailed experimental and mathematical analysis of real time chain kinetics initiated by low power laser pulses. The key advantages of the laser initiated chain reaction technique are: (1) the system is prepared in a well defined initial state on a time scale short with respect to the subsequent kinetics, (2) the full temporal evolution of the chain is monitored in real time, and (3) the radical densities, and thus the level of chain complexity, can be varied over several orders of magnitude by control of the photolysis pulse intensity. Consequently, the informative chain features of induction, propagation, and termination can be temporally resolved. Analysis of a complex chain reaction, intractable at steady state, is made accessible in quantitative detail. The method provides a nearly ideal kinetic framework for precise study of chain chemistry in the laboratory. It is worth noting that many important combustion systems proceed via branching rather than linear chain mechanisms. Our efforts to date have concentrated on linear chains, although the same techniques can be readily applied to branching systems as well.

In this paper we extend the laser initiated chain reaction technique to encompass a broad category of chain phenomena. The technique is applied to three chemical linear chain systems that provide contrasting kinetic examples of the generalized chain analysis. Section II contains a brief review of the experimental technique. In Sec. III, we investigate the kinetics of the previously unobserved, ultraslow Cl_2/HBr chain reaction, Cl' + HBr $\rightarrow Br' + HCl(v)$, $Br' + Cl_2 \rightarrow Cl' + BrCl$, where the second propagation step is 5. 68 kcal/mol endothermic¹⁹ and several orders of magnitude slower than the first propagation step (1 kcal=4. 18 kJ). This system is given as a

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model for chain reactions with extremely disparate propagation rates, and provides an excellent test of dynamic range and sensitivity of the technique. In Sec. IV, we present results for reactions of the two chemically distinct hydrogens in CH_3SH , each of which supports a chain. This multiple chain permits quantitative extension of the analysis of simpler chain reactions to complex systems more typical of realistic combustion phenomena. In Sec. V, we briefly investigate the intriguing time evolution of the Cl_2/H_2 chain reaction, in which the kinetics is complicated by a distribution of product states and by a finite delay time for appearance of HCl(v). This dark "induction" period is characteristic of many chain reactions, and contains detailed information on rates of the fundamental propagation processes.

II. EXPERIMENTAL

The experimental apparatus has been recently described in detail.¹⁸ Therefore, only a brief summary will be presented here, focusing primarily on additions to or modification of the existing apparatus for this series of experiments.

The apparatus consists of a pulsed laser, flow reactor cell, infrared detector, and signal averaging electronics. Short ultraviolet laser pulses are used to generate the initial Cl atoms by photodissociation of a small fraction of the molecular Cl2 in the flowing reagent mixture. The ultraviolet laser pulses are produced by either a frequency doubled, tunable dye laser $(2 \ \mu s/pulse, 1 \ mJ, 300 \ nm)$ or a frequency tripled, Qswitched Nd: YAG laser (5 ns/pulse, 1-40 mJ, 355 nm). Small fractions of the laser beam are used to trigger the electronics and monitor laser energy. The remaining laser light is beam expanded typically to a 5 cm diameter with a series of quartz lenses, corresponding to a laser fluence of $\leq 2 \times 10^{-3}$ J/cm² at even the highest laser powers. No differences are observed in the chain emission when using either the 2 μ s (500 W) or the 5 ns (8 MW) photolysis pulse, indicating the absence of any power dependent, multiphoton effects. The highly defocused photolysis pulse dissociates only a very small fraction $(\leq 10^{-4})$ of the parent Cl₂, ²⁰ thus ensuring that the chain kinetics occur in a strictly pseudo-first-order regime.

The flow cell (5, 0 cm diam \times 20 cm) is constructed entirely from quartz and is coated uniformly with halocarbon wax to minimize wall reactions. Nozzle inlets facing upstream into the flow provide rapid premixing of reagents in the argon buffer gas. Gas flows are measured with calibrated electronic flow meters and regulated with monel metering valves. Partial pressures of individual reagents are then calculated from relative flow rates and total cell pressure. Typical linear flow velocities in the cell are 20 cm/s; the gas mixture is thus continuously refreshed between laser pulses, eliminating effects from spatial propagation of the chain reaction upstream and pulse-to-pulse accumulation of products. The repetition rate of the laser is externally controlled from 0.1-10 Hz. The slower rates are used to prevent interference from chain exhaustion of reagents. In all the experiments described the results are found to be insensitive to a further twofold reduction in the laser pulse rate.

Infrared fluorescence signals from the chain product HCl(v) are observed as a function of time with a 77 K InSb large area infrared detector (1.48 cm²). Narrow bandpass interference filters are placed in front of the detector to select appropriate wavelengths of the emitting species and block stray light. Observation of $HCl(v \ge 2)$ is achieved by insertion of a 1 cm gas cell containing 100 Torr (1 Torr = 133.322 Pa) of HCl, which resonantly absorbs the $HCl(v = 1 \rightarrow 0)$ emission. The output from the detector undergoes two stages of amplification (×10⁵) and it digitized by a fast transient recorder (10 ns/ channel). The digitized signals from each laser are summed by a signal averager to enhance signal to noise and recorded.

III. Cl₂/HBr: A SLOW CHAIN REACTION

The Cl₂/HBr reaction system is of interest for two reasons. First, it is a surprise that any chain reaction proceeds at all. The fast propagation step, Cl' + HBr $\frac{b_1}{b_1}Br' + HCl(v)$, has been often studied to obtain the rate constant¹² and product state distribution.²¹ To the best of our knowledge, however, there has been no observation of the slow propagation step, $Br' + Cl_2 \stackrel{s_2}{\to} Cl' + BrCl_1$ that regenerates the initial CI atom and completes the chain cycle. Under appropriate experimental conditions, we can sensitively observe the steady state production of HCl(v) from this long-lived chain reaction (≥ 20 ms) that undoubtedly was present in the earlier studies as well. It is probable that many other chemical systems may sustain undesired and undetected chain reactions that can distort accurate analysis of the data. A more complete understanding of how to detect these slow chain reactions may help avoid some of these complications.

Second, this system provides an excellent test of the sensitivity and dynamic range of the laser initiated chain reaction technique. The Br⁺ + Cl₂ propagation step is 5. 68 kcal/mol endothermic and would be expected to be very slow. On the other hand, the Cl⁺ + HBr propagation step is very rapid. Chain reaction rate constants spanning such a wide range can be extremely difficult to measure accurately. A modification of the previous fast chain reaction analysis is presented for the Cl₂/HBr system; quantitative measurement of rate constant ratios in excess of 10^4 is demonstrated to be feasible.

Even in a chain reaction system as simple as Cl_2/HBr a complex manifold of radical-radical and radical-reagent processes can occur. The experimental method selects against nonlinear, radical-radical reactions by extreme defocusing of the photolysis pulse; only a very small fraction ($\leq 10^{-4}$) of the parent Cl_2 molecules is dissociated.¹⁸ The probability of radical-radical collisions is thereby drastically reduced; consequently, only pseudo-first-order radical-reagent processes need be considered. This simplifies the kinetic analysis, while retaining the important features of the main chain reaction system.

The relevant kinetic processes for the Cl_2/HBr system are the following:



FIG. 1. Typical data plot of HCl(v)chain emission from the slow Cl_2/HBr chain reaction system. The fast rise at early times is due to

 $Cl^{+} + HBr^{+} \rightarrow Br^{+} + HCl(v)$,

whereas the steady state emission at long times represents the recycling of the Br atoms via

$$\operatorname{Br}' + \operatorname{Cl}_2 \xrightarrow{n_2} \operatorname{Cl}' + \operatorname{Br}\operatorname{Cl}'$$

The relative intensities of the fast and slow emission components, in conjunction with τ_{decay} , is used to obtain the slow rate k_2 (see text).

 $\operatorname{Cl}_2 \xrightarrow{h\nu} \operatorname{Cl}^{\cdot} + \operatorname{Cl}^{\cdot} ;$ (1)

(2) Propagation,

Cl' + HBr $\stackrel{k_1}{\rightarrow}$ Br' + HCl(v), $\Delta H = -15.5 \text{ kcal/mol}^{19}$, (2)

Br' + Cl₂
$$\xrightarrow{\kappa_2}$$
 Cl' + BrCl, $\Delta H = 5.68 \text{ kcal/mol}^{19}$; (3)

(3) Vibrational deactivation,

$$\operatorname{HCl}(v) + M \xrightarrow{k_Q^{\alpha}} \operatorname{HCl} + M , \qquad M = \operatorname{HBr}, \operatorname{Cl}_2, \operatorname{Ar} ; \qquad (4)$$

(4) Termination,

$$Cl' - walls$$
, (5)

$$\mathbf{X}' + \mathbf{X}' + M \rightarrow \mathbf{X}\mathbf{X} + M, \quad \mathbf{X} = \mathrm{Br}, \mathrm{Cl}$$
 (7)

The duration of the Cl_2 photolysis pulse is much shorter than the time scale of the chain kinetics and thus can be considered as instantaneous. Buffer gas pressures (~5 Torr) are chosen to prevent diffusion of radical reaction species to the wall.⁵ Radical densities are controlled by the intensity of laser photolysis and chosen to make even gas kinetic radical-radical reaction processes negligible over the observed duration of the chain. Deactivation rates of HCl(v) by Ar,²² Cl_2 ,²³ and HBr^{24} have been previously measured.

Under these simplified conditions, the time dependence of the HCl(v) product is

$$[\operatorname{HCl}(v)(t)] = [\operatorname{HCl}(v)]_{0} \{ \exp(-t/\tau_{decay}) - \exp(-k_{1}[\operatorname{HBr}]) \} + [\operatorname{HCl}(v)]_{ss} [1 - \exp(-t/\tau_{decay})], \qquad (8)$$

where

$$[HCl(v)]_{0} = \frac{k_{1}[HBr][Cl]_{0}}{k_{1}[HBr] - (1/\tau_{decay})} , \qquad (9)$$

$$[HCl(v)]_{ss} = \frac{k_2[Cl_2][Cl]_0}{(1/\tau_{dec\,sr})} , \qquad (10)$$

$$\tau_{decay} = \left(\sum_{M} k_{Q}^{M}[M]\right)^{-1}.$$
(11)

Equation (8) can be interpreted in a straightforward fashion. At t = 0, the laser pulse generates an initial Cl atom concentration $[Cl]_0$, which in turn reacts with excess HBr to yield a rising exponential signal with rise time $\tau_{rise} = (k_1[HBr])^{-1}$. The overall rate of the chain reaction, however, is limited by the slow recycling of Br atoms by the second propagation step to reform Cl atoms. Consequently, the initial burst of $[HCl(v)]_0$, the "induction" feature, decays exponentially with τ_{decay} to a steady state level $[HCl(v)]_{ss}$. In this steady state regime almost all of the original Cl atoms have been exchanged for Br atoms; the finite HCl(v) concentration results from a balance between the slow regeneration of Cl atoms by the chain reaction and the rapid vibrational deactivation of HCl(v) by HBr.

A typical HCl(v) chain emission signal is shown in Fig. 1, which demonstrates excellent qualitative agreement with the above predictions. At early time there is a rapidly rising exponential induction feature due to the fast exothermic reaction $Cl' + HBr \stackrel{k_1}{\rightarrow} Br' + HCl(v)$, followed by vibrational deactivation to a steady state level of HCl(v) determined by the slow endothermic reaction $Br' + Cl_2 \stackrel{k_2}{\rightarrow} Cl' + BrCl$. On a much longer time scale $(\gtrsim 20 \text{ ms})$ the steady state chain emission decays to zero due to very slow, radical-radical termination pathways, reagent exhaustion, and bulk flow of the gas past the detector. This clean separation of chain reaction processes into distinct time scales is characteristic of the laser initiated chain reaction technique, and permits precise analysis of each rate process in isolation.

The first propagation step, $Cl' + HBr \stackrel{H}{\to} Br' + HCl(v)$, was briefly investigated by analysis of the fast rising exponential component of the emission. A series of data runs was taken varying [HBr] from 0.100 to 0.700 Torr, holding [Cl₂] at approximately 2.0 Torr. The value of τ_{rise} was determined by a least-squares exponential fit

(6)





of the difference between observed signal and the linearly back-extrapolated long time decay. In this case, the linear extrapolation introduces no error. A standard plot¹² of $(\tau_{rise})^{-1}$ versus P_{HBr} is a straight line of slope k_1 . Our data yield $k_1 = 7.9(\pm 1) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹, in excellent agreement with previous literature values of 8. 40(± 0.5) $\times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ and 7. 6(± 1.8) $\times 10^{-12}$ cm³ molecule⁻¹ s⁻¹. ¹²

The vibrational deactivation rate of HCl(v) is dominated by collisions with HBr and was measured from the post induction decay of the chain emission. The steady state HCl(v) signal was linearly extrapolated back to t=0. Differences between the decaying emission and the steady state base line were least-squares analyzed to generate τ_{decay} . A plot of $(\tau_{decay})^{-1}$ versus P_{HBr} was constructed, yielding $k_{Q}^{HBr} = (1.1 \pm 0.2) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹, again in good agreement with the literature value of $(1.04 \pm 0.1) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹.²⁴

Having analyzed the *fast* features of the signal, we now turn to the more subtle *slow* chain process. The slow propagation rate, $Br' + Cl_2 \stackrel{h_2}{\rightarrow} Cl' + BrCl$, can be obtained from the ratio of $[HCl(v)]_{ss}/[HCl(v)]_0$. This ratio should scale with the rate of Br atom recycling, and thus is en-

hanced for higher pressures of Cl_2 . A series of 19 data runs was taken holding $[Cl_2]$ at 8.0 Torr, varying [HBr] between 0 and 0.500 Torr. Both slow exponential decay and steady state emission signals were extrapolated to t=0 to obtain $[HCl(v)]_0$ and $[HCl(v)]_{ss}$, respectively (see Fig. 2). By Eqs. (9)-(11), a plot of $[HCl(v)]_{ss}/[HCl(v)]_0$ vs $[Cl_2] \cdot (\tau_{dscay} - 1/k_1[HBr])$ should be a straight line with slope k_2 . A plot of the data and a least-squares linear fit are presented in Fig. 2. The fit of the data to the linear model is good; a least-squares analysis yields $k_2 = (2.4 \pm 0.4) \times 10^{-15}$ cm³ molecule⁻¹ s⁻¹. This propagation rate is more than 3 000 times slower than the fast propagation rate, indicating the wide dynamic range accessible with the laser initiated chain reaction technique.

To the best of our knowledge, there is no prior experimental measurement of the extremely slow rate of Br' + Cl₂. However, the rate of the reverse reaction, Cl' + BrCl^{*-2} Br' + Cl₂, has been reported to be $k_{-2} = (1, 45 \pm 0, 2) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹.²⁵ The principle of detailed balancing can be used in conjunction with ther modynamic data¹⁹ to predict $k_2 = (2, 6 \pm 0, 4) \times 10^{-15}$ cm⁻³ molecule⁻¹ s⁻¹, which is in excellent agreement with our experimentally determined value.

The quantitative success of this analysis establishes the laser initiated chain reaction method as a reliable kinetic technique for measurement of chain propagation rates differing by up to four orders of magnitude. A further increase in experimental sensitivity by (i) integration of the steady state HCl(v) emission signals or (ii) time resolved laser induced fluorescence on the product BrCl promises to extend this limit by at least another order of magnitude.

IV. Cl_2/CH_3SH : A MULTIPLE CHAIN REACTION SYSTEM

In a complex combustion system, there are often several competing chain mechanisms present, ²⁶ which can enormously complicate the temporal evolution of the chain. Small changes in experimental conditions can thus significantly alter the chemical pathways, drastically changing the product composition. The Cl₂/CH₃SH chain system is unique in that it exhibits a number of parallel chain processes occurring simultaneously, with macroscopic branching steps that control the partitioning of chain radicals between the various mechanisms. The laser initiated chain reaction technique offers the opportunity to study this sophisticated, yet experimentally tractable, multiple chain reaction system in great detail. A precise understanding of this more complex model system promises to be of significant value in predicting the subtle kinetic behavior of corresponding combustion processes.

The relevant kinetic processes for the Cl_2/CH_3SH system are the following:

- (1) Pulsed initiation,
- $Cl_2 \stackrel{h\nu}{=} Cl' + Cl' ; \qquad (12)$

(2) Chain 1 propagation,

Cl' + CH₃SH
$$\stackrel{k_1}{=}$$
 CH₃S' + HCl(v), $\Delta H = -11.3$ kcal/mol, ^{19,27}
(13)

$$CH_3S' + Cl_2 \stackrel{h_2}{\longrightarrow} Cl' + CH_3SCl ; \qquad (14)$$

(3) Chain 2 propagation,

$$Cl^{*} + CH_{3}SH \xrightarrow{k_{1}} CH_{2}SH + HCl$$
, (15)

$$CH_{2}SH + Cl_{2} \xrightarrow{s_{2}} Cl' + ClCH_{2}SH ; \qquad (16)$$

(4) Cross chain propagation,

$$CH_{2}SH + CH_{3}SH \underset{k_{3}}{\stackrel{\leftrightarrow}{\leftarrow}} CH_{3}S' + CH_{3}SH ; \qquad (17)$$

(5) Vibrational deactivation,

$$HCl(v) + M \xrightarrow{k_{M}^{Q}} HCl + M$$
, $M = CH_{3}SH, Cl_{2}, Ar$. (18)

The interesting features of the Cl_2/CH_3SH system are evident in Eqs. (13)-(16). There are two different chain reactions operating on the two chemically distinct hydrogens in methanethiol. A hydrogen transfer reaction, Eq. (17), is included in the analysis for generality, interconverting the chain 1 and chain 2 radicals and thereby coupling the individual chains. Consistent with previous notation, the two pairs of chain propagation rates are labeled k_1 , k_2 , with primes to distinguish chain 1 (unprimed) from chain 2 (primed).

In the above kinetic scheme, all nonlinear radicalradical and diffusion termination processes can be neglected for reasons discussed in Sec. III. Even under these highly simplifying experimental conditions, the coupled differential equations are very tedious to manipulate. A solution requires specific concentrations of four time-dependent species [Cl', CH₃S', 'CH₂SH, and HCl(v) and, hence, the analytic inversion of the associated 4×4 rate matrix. Although this has been achieved with the assistance of the algebraic computer language macsyma, 28 the form of the general solution is sufficiently complex to render interpretation of the kinetics difficult. Two approximations, however, simplify the solution considerably. First, the chain 1 propagation rates have been previously measured¹ to be $k_1 = (1, 8)$ ± 0.4 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹, and $k_2 = (1.1 \pm 0.2)$ $\times 10^{-11}$ cm³ molecule⁻¹ s⁻¹, both large. Provided that the chain 2 propagation rates, k'_1 and k'_2 , are substantially slower, one can decouple to first order the temporal evolution of the two chain reactions. This amounts to assuming that chain 1 reaches steady state long before chain 2, an assumption that will be experimentally verified. Second, the hydrogen transfer reaction, Eq. (17), can be expected to have an appreciable rate only in the exothermic direction. From previous studies in an arrested relaxation apparatus, 27 it has been suggested that the S-H bond is ~6 kcal/mol weaker than the C-H bond. Thus we can safely neglect the reverse reaction in Eq. (17), setting $k_{3} \approx 0$. It is worth noting that up until these assumptions are made, the kinetic solution is strictly symmetric with respect to chain 1 and chain 2. However, the greater exothermicity of chain 1 as a result of the weaker S-H bond is consistent with our assignment of the fast chain processes to k_1 and k_2 . Note also that the HCl produced via reaction (15) is not vibrationally hot, due to similar exothermicity considerations. This, in fact, affects only the *intensity* of the observed emission, since the time dependent production of HCl(v) is determined solely by [Cl(t)].

In this limit, the predicted time dependence of HCl(v) simplifies to

$$[\operatorname{HCl}(v)(t)] \simeq A[1 - \exp(-t/\tau_1)]$$

+
$$B[1 - \exp(-t/\tau_2)] + C[1 - \exp(-t/\tau_3)]$$
,
(19)

where the exponential time constants are

$$\tau_1 = (k_1[CH_3SH] + k_2[Cl_2])^{-1}, \qquad (20)$$

$$\tau_2 = \left(\sum_{\boldsymbol{M}} k_{\boldsymbol{Q}}^{\boldsymbol{M}}[\boldsymbol{M}]\right)^{-1}, \qquad (21)$$

$$\tau_{3} = k_{3}[CH_{3}SH] + k_{2}'[Cl_{2}] + \frac{k_{1}'[CH_{3}SH]}{1 + \frac{k_{1}}{k_{2}} \frac{[CH_{3}SH]}{[Cl_{2}]}}, \qquad (22)$$

and the pre-exponential factors are given by

$$A = \frac{(k_1[CH_3SH])^2[C1]_0}{(1/\tau_1)(1/\tau_1 - 1/\tau_2)} , \qquad (23)$$

$$A + B = \frac{k_1 [CH_3SH] k_2 [Cl_2] [Cl]_0}{(1/\tau_1)(1/\tau_2)} , \qquad (24)$$

$$A + B + C = \frac{k_1 [CH_3SH]k_2 [Cl_2] [Cl]_0}{(1/\tau_1)(1/\tau_2)} \times \frac{(k_2' [Cl_2] + k_3 [CH_3SH])}{(1/\tau_3)}.$$
(25)

In Eqs. (23)-(25) the progressive sums are listed, since they correspond to the experimentally observed emission amplitudes for early, intermediate, and steady state time regions (see Fig. 3). One should note that the above solution has only three independent time constants. Mathematically, this implies that the 4×4 rate matrix has one zero eigenvalue. In more physical terms, this means that there is an extra constraint linking the radical concentrations, i. e., the *total* radical concentration is a conserved quantity throughout the chain reaction under the conditions of the analysis.

The time development of HCl(v) [Eq. (19)] can be readily interpreted. The first exponential term corresponds to the induction period of chain 1; at early times $(t < \tau_1)$ there is a burst of HCl(v) as the original excess of Cl atoms come into steady state with CH_3S' radicals. The second exponential term describes the subsequent steady state evolution of chain 1 under the influence of vibrational deactivation by CH_3SH , Cl_2 , and Ar. Finally, the third exponential term represents the much longer induction period of chain 2, whereby the Cl atoms begin to cooperate in another chain mechanism by means of propagation rate k'_1 . Eventually, the rates of interconversion of Cl', CH_3S' , and CH_2SH balance, and a finite concentration of HCl(v) is dynamically maintained.

Typical data are shown in Fig. 3, demonstrating excellent qualitative agreement with the kinetic predictions. At very early times [Fig. 3(a)], the sharply rising chain 1 induction feature is cleanly observed, followed by a prolonged rise corresponding to steady state production of HCl(v). On a longer time scale [Fig. 3(b)], the indirect conversion of CH_3S' to $'CH_2SH$ takes place via the chain 2 propagation reactions (15)



FIG. 3. HCl(v) product emission from the Cl₂/CH₃SH multiple chain reaction, demonstrating the predicted triple exponential rise and decay. At early times (a) there is a rapid burst of HCl(v) corresponding to the induction period of chain 1, followed by a slower rise due to competition between propagation and vibrational deactivation. At long times (b), the slower chain 2 eventually "siphons" chain radicals away from chain 1, resulting in a decreased, steady state HCl(v) emission intensity. [HCl(v)]_{es} and $[HCl(v)]'_{ss}$ emission amplitudes are obtained by extrapolating to t = 0 the intermediate and steady state signals.

and (16), with a commensurate reduction in HCl(v) emission as the much slower chain 2 begins to predominate. Ultimately, a steady state of both chains 1 and 2 is attained, resulting in constant HCl(v) emission, which slowly decays due to termination processes neglected in the analysis. It is interesting to note that in such a multiple chain reaction system, the overall production is eventually dominated by the *slower* of the parallel chain processes, since it is that process that tends to accumulate the chain radicals.

In such a complex system, the laser initiated chain reaction technique can extract a wealth of quantitative kinetic information from both the intensity and temporal evolution of the signals. Detailed measurements of the initial fast chain have been described elsewhere.¹ In this treatment, we focus on the important aspects of the second slow chain.

The key features of the multiple chain kinetics are contained in (i) τ_3 , the slow induction time for chain 2, and (ii) the ratio of HCl(v) steady state emission amplitudes *before* and *after* this second chain induction period, designated as $[HCl(v)]_{se}$ and $[HCl(v)]_{se}'$. From the kinetic solution, these amplitudes are given by Eqs. (24)-(25) as A+B, and A+B+C, respectively. Experimentally, they are obtained by back extrapolating the intermediate and long time HCl(v) emission signals to t=0 (see Fig. 3). Since we are only interested in the ratio of these signals, all difficulties associated with an absolute measurement of their concentrations are avoided.

Experimentally one determines $[HCl(v)]'_{ss}/[HCl(v)]_{ss}$ and τ_3 ; the known kinetic solutions for these quantities Eqs. (22), (24), and (25) can be manipulated into a form appropriate for extracting the desired rate constants:

$$\frac{\mathrm{HCl}(v)]_{\mathrm{ss}}}{\mathrm{HCl}(v)]_{\mathrm{ss}}} \cdot \frac{1}{\tau_{3}[\mathrm{CH}_{3}\mathrm{SH}]} = k_{2}' \frac{[\mathrm{Cl}_{2}]}{[\mathrm{CH}_{3}\mathrm{SH}]} + k_{3} , \qquad (26)$$

$$\left(\frac{1}{\tau_{3}[C1]_{2}}-k_{2}'-k_{3}\frac{[CH_{3}SH]}{[Cl_{2}]}\right)^{-1}=\frac{1}{k_{1}'}\frac{[Cl_{2}]}{[CH_{3}SH]}+\frac{k_{1}/k_{2}}{k_{1}'}.$$
(27)

A plot of the left-hand side of Eq. (26) versus $[Cl_2]/$

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FIG. 4. Chain data plots for the Cl_2/CH_3SH multiple chain reaction system: (a) relative intensities of chain 1 and chain 2 steady state emission; (b) chain 2 induction time constant. From these straight line fits rate information on k'_1 , k'_2 , k_3 , and k_1/k_2 is obtained (see the text for kinetics).

[CH₃SH] should yield a straight line of slope k'_2 and intercept k_3 . These experimentally determined rate constants can then be used in Eq. (27) to generate another straight line kinetic plot, with slope $1/k'_1$ and intercept $(k_1/k_2)/k'_1$. This procedure both avoids the intrinsic numerical instabilities associated with a four-parameter nonlinear fitting scheme and displays the data in straight line plots more readily evaluated for quality of fit.

A total of 13 data runs was taken varying $[CH_3SH]$ from 0. 20 to 2.5 Torr, with $[Cl_2]$ held approximately constant at 2.0 Torr. The long time, steady state emission signals were extrapolated to t=0, generating $[HCl(v)]'_{ss}$ as well as the sloping base line for the slow, chain 2 induction decay τ_3 [see Fig. 3(b)]. This decay was least-squares fitted to an exponential and back extrapolated to t=0, extracting the value for τ_3 and $[HCl(v)]'_{ss}$. An intensity data plot of

$[\operatorname{HCl}(v)]'_{ss}$	1		$[Cl_2]$
$[\mathrm{HCl}(v)]_{\mathrm{ss}}$	$ au_{3}[CH_{3}SH]$	vs	[CH ₃ SH]

is shown in Fig. 4(a). A linear relation fits the data well, in agreement with the above predictions. Least-squares analysis of the slope yields $k'_2 = (2.6 \pm 0.3) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹. The intercept (i. e., the rate k_3) is equal to zero within the uncertainty of the fit. We can therefore set an upper bound on $k_3 \gtrsim 1 \times 10^{-15}$ cm⁸ mole-cule⁻¹ s⁻¹, i. e., bimolecular interconversion of the chain radicals appears to be negligible over the experimental range investigated. With k'_2 and k_3 thus determined, a second plot of

$$\left(\frac{1}{\tau_{3}[\text{Cl}_{2}]} - k_{2}' - k_{3} \frac{[\text{CH}_{3}\text{SH}]}{[\text{Cl}_{2}]}\right)^{-1} \text{vs} \frac{[\text{Cl}_{2}]}{[\text{CH}_{3}\text{SH}]}$$

can be constructed, and is shown in Fig. 4(b). Again the linear fit is very good, further supporting the proposed multiple chain kinetic analysis. Least-squares determination of slope and intercept yield $k'_1 = (4.3 \pm 1)$ $\times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ and $k_1/k_2 = (11 \pm 5)$. The measured value for k_1/k_2 , the ratio of chain 1 propagation rate constants, is in reasonable agreement with previous measurements $k_1/k_2 = (16 \pm 3)$. To the best of our knowledge, there has been no previous determination of k'_1 , the rate for abstraction of methyl hydrogens from CH₃SH by Cl radicals. This is not surprising since k_1 , the corresponding rate for the much weaker S-H bond, is almost 50 times faster and would dominate the reaction pathways in a standard flow tube study of isolated radical kinetics. The laser initiated chain reaction method may be one of the only convenient ways to measure such rate constants directly. The value for k'_1 is between the known rates of hydrogen abstraction from methane²⁹ $[(1.12 \pm 0.3) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$ and methanol³⁰ $[(6.3 \pm 0.7) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$, as might be expected from simple bond strength arguments.^{27,31}

It should be noted that the kinetic expressions (26) and (27) are purposefully overspecified, i.e., the values obtained from a best fit to Eq. (26) need not necessarily fit Eq. (27). The agreement between the two fitted data plots, therefore, bolsters the kinetic theory developed in this section and highlights the laser initiated chain reaction technique as a method for generating quantitative insight into complex chain combustion phenomena.

V. Cl₂/H₂: A SLOW STARTING CHAIN REACTION SYSTEM

In all the systems investigated by the laser initiated chain reaction technique thus far, the initial rapid "equilibration" of the chain radicals has generated HCl(v) at a rate *faster* than can be maintained at steady state. As a result, the chain emission at early times demonstrates a sharply rising *positive* induction feature with a finite derivative at t=0. This is a direct and obvious consequence of the fact that the vibrationally excited HCl(v) is the product of the *first* propagation reaction. The observed product of transient combustion often results from a sequence of propagation reactions and a slowly rising, sigmoidal time development of the product is predicted. Typically, however, this induction feature occurs so rapidly that it cannot be temporally resolved by previous methods of chain investigation. But chain initiation by the pulsed laser prepares the system (i.e., photolytically generates the necessary chain radicals) on a time scale much shorter than the mean free time between collisions. Consequently, the interesting and informative induction kinetics can be observed even for gas kinetic chain processes.

The Cl_2/H_2 chain system, initiated by photolysis of Cl_2 , is perhaps the simplest example of a rapid chain reaction with product emission that "turns on" gradually with a time resolved, sigmoidally rising induction feature. In this section we present results of a brief qualitative investigation of this phenomenon, as well as a discussion of experimental subtleties for quantitative kinetic analysis of chain emission from multiple vibrational states.

The relevant chemical processes in the Cl_2/H_2 chain system are (1) propagation,

$$Cl' + H_2 \stackrel{R_1}{\longrightarrow} H' + HCl(v=0)$$
, $\Delta H = 1.2 \text{ kcal/mol}^{19}$, (28)

$$H' + Cl_2 \xrightarrow{s_2(v)} Cl' + HCl(v) , \qquad \Delta H = -45.2 \text{ kcal/mol}^{19} , \qquad (29)$$

for v = 0-5, and (2) vibrational deactivation,

$$\operatorname{HCl}(v) + M \xrightarrow{k_{Q}^{M}(v, v')} \operatorname{HCl}(v') + M , \qquad (30)$$

where $M = H_2$, Cl_2 , Ar and v, v' = (0, 1, 2, 3, 4, 5).

Over the time scale of the induction feature, any effects from termination are negligible. Due to the long Cl_2/H_2 chain length, however, the bulk gas flow (20 cm/s), laser beam diameter (5 cm), and pulse repetition rate (0.1 Hz) need to be chosen carefully to eliminate interference from pulse-to-pulse accumulation.

The observed HCI(v) emission arises solely from reaction of the H atoms, the time dependence of which is readily found to be

$$[H(t)] = \frac{k_1[H_2][Cl]_0}{k_1[H_2] + k_2[Cl_2]} \times (1 - \exp\{-(k_1[H_2] + k_2[Cl_2])t\}), \qquad (31)$$

where k_2 is defined as the total production rate for all vibrational states, $\sum_{v} k_2(v)$. By Eq. (31), the concentration of H atoms is initially zero, rising exponentially to a steady state value with an induction time τ_{ind} = $(k_1[H_2] + k_2[Cl_2])^{-1}$. As is generally the case, the induction time is determined by the *sum* of both propagation rates. The H atoms are continuously reacting with excess $[Cl_2]$ to form HCl(v), whose time development is determined by the set of equations

$$\frac{d[\text{HC1}(v)(t)]}{dt} = k_2(v)[\text{Cl}_2][\text{H}(t)] -\sum_{v'} k_Q^M(v, v')[M][\text{HC1}(v)(t)], \qquad (32)$$

where v = (0, 1, 2, ..., 5). An exact solution of this coupled system for all vibrational levels requires the analytic diagonalization of a 6×6 rate matrix. However, for early time when the concentrations of HCl(v) for all v are small, the coupling terms in Eq. (32) are negligible, i. e., the quenching rates are very much slower than chain progagation, and the solution can be found by simple integration:

$$[HCl(v)(t)] = k_{chain}t - [HCl(v)]_{ind} \\ \times (1 - \exp\{-(k_1[H_2] + k_2[Cl_2])t\}), \qquad (33)$$

$$k_{\text{chain}} = \frac{k_1[H_2]k_2[Cl_2][Cl]_0}{k_1[H_2] + k_2[Cl_2]} , \qquad (34)$$

$$[\text{HCl}(v)]_{\text{ind}} = \frac{k_1[\text{H}_2]k_2(v)[\text{Cl}_2][\text{Cl}_3]}{\{k_1[\text{H}_2] + k_2[\text{Cl}_2]\}^2} , \quad v = (0, 1, 2, 3, 4, 5) .$$
(35)

These equations lend themselves to simple interpretation. For very early times $(t \ll \tau_{ind})$ [H(t)], and therefore the rate of production of HCl(v), is essentially zero. During the induction period $(t \sim \tau_{ind})$, the rate of production of HCl(v) increases as more H atoms are produced, resulting in an upward curving signal. Eventually $(t \gg \tau_{ind})$, the concentration of H atoms comes to a steady state and the vibrationally excited HCl(v) grows linearly with time. The net amplitude of HCl(v), however, is lower by an amount [HCl]_{ind} than it would have



FIG. 5. Typical emission data from the Cl_2/H_2 chain reaction, demonstrating the gradual rather than prompt appearance of HCl (v) product predicted by the kinetics. The spike at t=0 is due to window fluorescence from the laser pulse and indicates the response time of the detector. Note the disparate pressures of H₂ and Cl₂ required to ensure maximum visibility of the sigmoidal rise.

been had no time been "lost" attaining steady state.

A sample data run is presented in Fig. 5, clearly demonstrating the anticipated sigmoidal rise of HCl(v)emission. Although such a feature is mathematically predicted for all pressures of $[Cl_2]$ and $[H_2]$, the magnitude of the effect can be shown from Eq. (35) to be maximum for $k_1[H_2] = k_2[Cl_2]$. The rate k_1 , ³² however, is approximately one thousand times slower than k_2 , ³³ and hence extremely large $[H_2]/[Cl_2]$ ratios are necessary to ensure greatest visibility of the sigmoidal induction feature.

A precise description of the post induction kinetics is by no means as simple, requiring a rigorous solution of Eq. (32). The key point is that for *early* times, all the different vibrational product HCl states are governed by the *same* kinetic differential equation, while for *later* times *each vibrational state evolves differently*. Unavoidably, the full solution for each vibrational state contains many exponential time components, corresponding to collisional cascading from the upper to lower levels. In the simple Landau-Teller model,³⁴ harmonic oscillator deactivation probabilities access only adjacent states and scale with radiative transition strength, i.e., linearly with vibrational quantum number. Based on this model, Montroll and Schuler³⁵ were able to prove that total emission from an arbitrarily prepared ensemble of oscillators appears to decay with a single exponential lifetime and, in particular, the lifetime of the v = 1 - 0 deactivation. Consequently, although the full solution to Eq. (32) for each vibrational state is extremely complex, the summed emission behaves like a simple exponential decay owing to fortuitous cancellation.

The presence of these various exponential components hidden in the total emission is experimentally verified in Fig. 6, where the laser initiated Cl_2/H_2 chain emis-



FIG. 6. HCl (v) emission from the Cl₂/ H₂ chain system, demonstrating the presence of multiple exponential decay parameters. The smooth curve represents total HCl (v) emission viewed through a wide band filter. The noisier curve (multiplied by 10) is the emission viewed through a narrow band filter passing predominantly HCl $(v = 5 \rightarrow 4)$, which exhibits a much more rapid rise time.

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sion is viewed through (i) a broad band filter that passes all HCl(v - v - 1) transitions, and (ii) a narrow band filter that passes predominantly HCl(v = 5 - 4). The emission through the narrow band filter, sampling mainly the higher vibrational states, shows a much faster rise time (i. e., more rapid vibrational deactivation rate) than when all transitions are viewed.

Deactivation rates of HCl(v) have been measured for v = 1-5, and are found to deviate substantially from the simple, linear Landau-Teller prediction.³⁶ Recent experimental and theoretical studies of some highly excited diatomics indicate that deactivation mechanisms can involve rapid, highly nonresonant V-T, R processes³⁷ and that rates empirically scale as a power law in vibrational quantum number.^{38,39} The effects of such major departures from the Landau-Teller model have been theoretically investigated⁴⁰ and shown to produce nonsingle exponential behavior. Thus, extracting quantitative rate data from the inhomogeneous emission of a product state distribution requires very careful consideration in the analysis.

VI. CONCLUSION AND SUMMARY

The laser initiated chain reaction technique, in conjunction with state-of-the-art infrared detection, provides a new approach to quantitative chain analysis. The extensions of the technique presented in this paper permit detailed investigation of a much broader class of chain reaction systems. Chain reactions with propagation rate constant ratios in excess of 10^4 can be directly studied via the measurement of peak to steady state product emission signals. Analysis of the Cl₂/HBr chain system indicates the presence of an ultraslow, second propagation step, $Br' + Cl_2 \stackrel{h_2}{\rightarrow} Cl' + BrCl$, which has been previously unobserved and yet undoubtedly present in earlier studies of the $Cl' + HBr \stackrel{R_1}{\rightarrow} Br' + HCl(v)$ reaction. A complex multiple chain reaction is observed in the Cl_2/CH_3SH system, where each of two chemically distinct hydrogens supports simultaneous, coupled chain reactions. The laser initiated chain reaction technique is found ideally suited to probe such a system, allowing all stages of a complex chain (i. e., the coupled induction and propagation steps) to be resolved temporally and readily analyzed. The additional interesting effect of chain radical accumulation in the slower of the two parallel chains is experimentally verified. The unique capability of the technique to capture accurately the fast induction kinetics is tested on the Cl₂/H₂ system, where a sigmoidal, slowly rising induction feature is predicted and observed.

The extended chain analysis presented in this paper accommodates systems of considerable complexity by experimental manipulation of radical densities into a regime where the kinetics become simplified. Once a detailed understanding of the fundamental, intrinsic chemistry is obtained, the radical densities can be continuously increased to enhance higher order, radicalradical reactions that become important in bulk combustion. Further research in these directions will ultimately help bridge the gap between our understanding of isolated radical chemistry and more complex combustion phenomena.

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