PULSED KINETIC STUDIES OF LASER EXCITED MOLECULAR STATES

by

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Abstract

A tunable pulsed dye laser is used to study reactions of atoms and molecules in their ground and electronically excited states. Infrared detection of vibrational fluorescence serves to monitor reaction rates and branching ratios of reaction exothermicity. Studies of the reaction Cl₂ + H₂S have been carried out using Cl₂ and S₂Cl₂ as photodissociation sources of Cl₂ atoms. The reaction with Cl₂ as a source of Cl₂ is shown to proceed via a further chain reaction. The HCl product of the Cl₂ + H₂S reaction is vibrational excited (v=1), while the HS product is not. The analogous reaction of Br²(2P₁/₂) + H₂S is found to produce HBr(v=1) predominantly. Studies of this kind provide a wealth of new information about the dynamics of the reactive collisions in simple systems.

Introduction

There has been considerable interest in the reactions of chlorine atoms for theoretical understanding of the dynamics of atom-diatomic reactions, in chemical lasers and in their reactions with species present in the stratospheric ozone layer. These processes have been studied by mass spectrometry-flow discharge techniques, resonance absorption, resonance fluorescence, infrared chemiluminescence, crossed molecular beams as well as laser-initiated chemiluminescence. In the present study we report the first measurement of the absolute rate constant for the reaction of atomic chlorine with H₂S, using the technique of laser initiated chemiluminescence. Contrary to a previous investigation, we also demonstrate that in a chemical laser based on Cl₂/H₂S a chain mechanism contributes to the kinetics of the system.

The electronic to vibrational (E→V) energy transfer in systems containing Br²(2P₁/₂) and I²(2P₁/₂) has been extensively studied by several workers. Here, we report a preliminary investigation of the novel case of the Br²(2P₁/₂)/H₂S system where both chemical reaction and E→V energy transfer can take place.

Experimental

The apparatus consists of a gas handling and storage system, flow lines and a quartz reaction vessel with laser photoexcitation and infrared detection equipment.

The gas handling system is comprised of pyrex storage bulbs and tubing. Stopcocks with Buna 'O' rings coated with a Teflon based grease are used throughout the system. The gases used in these experiments with the manufacturer's purity were as follows: Ar (99.999%), HCl (99%), HBr (99.8%), H₂S (99.9%) and Cl₂ (99.96%); Br₂ (99.8%) and S₂Cl₂ (99%) were supplied as liquids. With the exception of the Ar diluent gas, all reagents were degassed at 77°K several times before being distilled into a-storage bulb at a few torr vapor pressure, only the middle fraction of the distillate being retained.

The gas fore-pressures were measured with monel Bourdon gauges. Flows were monitored with ball flowmeters or electronic capacitance mass flowmeters and were controlled by stainless steel or monel needle valves. Flow calibrations were periodically rechecked. Typical experimental flow conditions are given in Table I.

A schematic of the experimental arrangement is shown in Fig. 1. The reaction flow tube consists of a quartz vessel of 1 1/4" diameter with infrasil windows sealed on at the sides and a 1" sapphire

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Fig. 1. Experimental Apparatus for Dynamic Studies of Reactive and Excited Species. A pulsed dye laser, collimated by a quartz lens, is focused into a multiple pass cell. An InSb detector is mounted above the reaction cell at right angles to the incident beam. The signal from the detector is amplified and captured by a transient digitizer, when triggered by a photodiode from scattered laser light. The signal is then stored in a signal averager/computer and subsequently retrieved in a plot either on an oscilloscope or plotter.

window attached with black wax on the top for transmission of infrared radiation. Pressures in the reaction vessel are measured with a pressure transducer.

Halogen atoms are produced in pulses by photolysis using a commercial flashlamp-pumped dye laser. For the case of C\textsubscript{2} atom production the laser is frequency doubled and with Rhodamine 6G, 300 nm light pulses of 1 mJ and 2 µsec are obtained. Br\textsuperscript{2} is generated by the photolysis of Br\textsubscript{2} using a variety of blue green dyes; typically pulses of 10 mJ and 1 µsec duration are produced.

A multiple pass arrangement consisting of dielectric coated mirrors is employed to enhance the signal. The laser beam is collimated before the multiple pass by a quartz lens of focal length 50 cm.

For a typical reaction,

\[ X + HYH \rightarrow HX^+ + HY^+ \]

where \(^+\) denotes vibrational excitation, the progress of the reaction is monitored by observation of the time resolved infrared fluorescence of the vibrationally excited product molecules. A signal thus obtained consists of a rapidly rising portion, the risetime, corresponding to the rate of product formation, followed by a slow decay due to the vibrational relaxation of the excited product molecules. In the majority of experiments a large area InSb detector with appropriate interference filter placed over the element, is mounted directly above the reaction cell. Where a gas filter cell is required, a CaF\textsubscript{2} (f/1) lens is placed above the reaction vessel and a 10 cm gas cell is inserted between the lens and the detector.

The signal (emission amplitude vs. time) from the detector is passed through a 100 kHz RC cut-off filter and into a wide band amplifier. The signal is subsequently stored in a transient digitizer (±10 nsec/pt.) and the digital information transferred to a signal averager/computer. Typically 1000 channels of data are acquired at a repetition rate of 20 Hz for up to 60 seconds. A typical set of
Chemiluminescence traces is shown in Fig. 2.

Linear semi-logarithmic plots of amplitude vs. time are obtained from the risetime signal as determined from the difference between the observed risetime trace and an extrapolation of the decay trace. From these plots, the time constant of the rise is determined. In the case of the faster risetimes ($\tau < 10 \mu$sec), the finite risetime of the detection system (1.75 $\mu$sec) required that a correction be made to the observed risetime of the signal such that

$$\tau_{\text{real}} = \left( \frac{\tau^2_{\text{observed}} - \tau^2_{\text{apparatus}}}{2} \right)^{1/2}$$

Results and Discussion

A. The reaction of Cl + H$_2$S

The primary aim of these experiments was to investigate the energy channeling of the reaction exothermicity in the reaction

$$\text{Cl} + \text{H}_2\text{S} \rightarrow \text{HCl} + \text{HS} \quad \Delta H = -12 \text{ kcal/mole} \quad (1)$$

as well as to determine the reaction rate. The exothermicity of (1) is sufficient only to produce either HCl or HS in the ($v=1$) state in each reactive encounter. Therefore the partitioning of reaction exothermicity between the two product molecules will provide important information about the reactive dynamics.

In the earlier work of Pritt et al.$^{13}$ on the Cl$_2$/H$_2$S chemical laser, they postulated that there
was no chain reaction mechanism following reaction (1). In preliminary investigations using Cl₂ as a source of Cl atoms we have compared the intensity of reaction (1) to the reaction:

\[ \text{Cl} + \text{HBr} \rightarrow \text{HCl}^+ + \text{Br} \quad \Delta H = -15.5 \text{ kcal/mole} \quad (2) \]

The total signal intensity observed from reaction (1) was ≈50 times that produced in (2). Since it had been previously determined by Polanyi et al.⁷ that 50% of the available energy in reaction (2) goes into vibrationally excited HCl, we conclude that a chain mechanism must be operative in the Cl₂/H₂S system.

Using Cl₂ as a source of Cl, the most likely mechanism appears to be:

\[ \text{Cl}_2 \xrightarrow{h\nu, 300 \text{ nm}} 2\text{Cl} \]
\[ \text{Cl} + \text{H}_2\text{S} \rightarrow \text{HCl} + \text{HS} \quad \Delta H = -12 \text{ kcal/mole} \quad (3) \]
\[ \text{HS} + \text{Cl}_2 \rightarrow \text{HSCl} + \text{Cl} \quad \Delta H = -2 \text{ kcal/mole} \]
\[ \text{Cl}_2 + \text{HSCl} \rightarrow \text{HCl} + \text{SCl}_2 \quad \Delta H = -30 \text{ kcal/mole} \quad (4) \]

With the use of an HCl gas filter (50 torr, 10 cm pathlength), to block the HCl(v=1=0) emission entirely, it was noted that 50% of the signal arises from an excited species other than HCl(v=1). Because only a wide band interference filter was available, we were only able to conclude that the emitting species is either HCl(v>1) from reaction (4) or HS(v=1) from reaction (1).

Under the conditions of these experiments, the signal from an individual vibrationally excited species is inversely proportional to its radiative lifetime. A recent ab initio calculation indicates that the lifetime for HS(v=1) is ≈10 times longer than that of HCl(v=1).¹⁴ Since the HS produced in reaction (1) is also being rapidly consumed by reaction (3), we can conclude further that the excited species we observed other than HCl(v=1) was HCl(v>1) from reaction (4).

S₂Cl₂ was used as an alternative photodissociation source of Cl atoms, this source being found unreactive with HS, and thus preventing the chain mechanism. The photochemistry of S₂Cl₂ in the near ultraviolet is not well understood. A number of photodissociation products have been observed following the flash photolysis of S₂Cl₂ in the ultraviolet. Donovan et al.¹⁵ have suggested that under their conditions of photolysis (λ > 1800 or 2000 Å, 0.3 torr S₂Cl₂, 500 torr N₂, E = 1600 J) the major primary product was SCl₂. Under the conditions employed in these experiments, as given in Table 1, with photodissociation of S₂Cl₂ at 300 nm, reactions characteristic of Cl atoms have been observed both with HBr and H₂S. Secondly, no other primary photolysis fragments would show similar behavior in producing the HCl⁺ product. Secondary products resulting from reactions of SCl₂ would not contribute to the kinetics in our experiments because of the low reagent pressures used and the relatively

<table>
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<th>Gas</th>
<th>Flow (µmoles/sec)</th>
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<tr>
<td>Argon</td>
<td>235</td>
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<tr>
<td>S₂Cl₂/Argon (10%)</td>
<td>3</td>
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<tr>
<td>H₂S/Argon (10%)</td>
<td>5</td>
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<table>
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<tr>
<th>Gas</th>
<th>Typical Pressure (torr)</th>
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<tbody>
<tr>
<td>Argon</td>
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<tr>
<td>H₂S</td>
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</tr>
<tr>
<td>S₂Cl₂</td>
<td>0.05</td>
</tr>
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</table>
short time duration of the experiment. We conclude that a major photolysis channel under the conditions employed in the present work is the process

$$\text{S}_2\text{Cl}_2 \xrightarrow{\text{hv}} 300 \text{ nm} \quad \text{S}_2\text{Cl} + \text{Cl}$$

Similar experiments to the ones carried out with Cl$_2$ as a source of Cl atoms were repeated with S$_2$Cl$_2$. The entire chemiluminescence signal was found to be attenuated by the HC$I$ gas filter and the HC$I$ signal amplitude of the Cl+$\text{H}_2\text{S}$ reaction was of the same magnitude as for Cl+$\text{HBr}$. We therefore concluded that the HS chain reactions (3) and (4) are prevented when S$_2$Cl$_2$ is used as the photolysis source. Thus we were able to study the basic atom-triatom reaction (1) carefully in the absence of the obscuring chain effects.

A number of rate measurement experiments were carried out over a range of H$_2$S pressures ($0 \leq P \leq 0.2 \text{ torr}$) and a plot of these results is given in Fig. 3. With an error of two standard deviations the rate constant of the reaction for Cl+$\text{H}_2\text{S}$ was found to be exceedingly rapid,

$$k = 6.0 \pm 0.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$$

From comparison with the data for the Cl+$\text{HBr}$ reaction it was determined that ~80% of the available energy in reaction (1) appears as vibrational excitation in the HC$I$ product. From the absence of any signal from HS(v=1) and its computed radiative lifetime we estimate that HS is excited to v=1 less than 5% of the time.

Because of the rapid dynamics involved in the Cl+$\text{H}_2\text{S}$ reaction and the relatively small role the HS fragment appears to play in the channeling of reaction exothermicity, an analogy can be made between this process and a typical atom-diatom encounter, e.g.,

$$\text{H} + \text{LH} \xrightarrow{} \text{LH} + \text{H} \quad (\text{L} = \text{light}, \text{H} = \text{heavy atoms})$$

In this case, much of the reaction exothermicity is deposited in the newly formed bond. Since the Cl+$\text{H}_2\text{S}$ reaction is very rapid, it is concluded that the barrier height to reaction is relatively small and the possibility of energy exchange between HC$I$ and HS after reaction by secondary encounters is unlikely. Polanyi et al. have done trajectory calculations for the process

$$\text{Cl} + \text{HI} \rightarrow \text{HCl} + \text{I} \quad \Delta H = -31.7 \text{ kcal/mole}$$

using a LEPS interaction potential. They found that efficient vibrational excitation in the HC$I$ product takes place on an energy surface with a repulsive barrier early in the entrance channel of the reaction. We postulate that the Cl+$\text{H}_2\text{S}$ reaction behaves similarly and that the internal degree of freedom of the HS vibration has very little effect on the dynamics of the reaction. This is very similar to the results found for many other atom-triatom reactions reported in the literature. Possible additional uptake of energy as rotation in the HS fragment awaits more detailed calculations.

![Fig. 3. Experimental data for the reaction of Cl+$\text{H}_2\text{S}$. The inverse of the lifetime for the formation of HC$I$ is plotted against H$_2$S pressure for a range of pressures. The rate constant is determined from the slope of the plot.](image_url)
B. The reaction of \( \text{Br}^*(2P_{1/2}) + \text{H}_2\text{S} \)

The investigation of the \( \text{Br}^* + \text{H}_2\text{S} \) reaction is in its preliminary stages and only an outline of the results will be given here.

Figure 4 illustrates the possible channels that exist both for reaction and E-V energy transfer in this system. Experimentally we found that the reaction between ground state \( \text{Br}(2P_{3/2}) \) and \( \text{H}_2\text{S} \) yields no vibrationally excited products. \( \text{Br}_2 \) was photolysed at 560 nm to produce two ground state atoms. No signal was seen from the \( \text{Br} + \text{H}_2\text{S} \) reaction relative to a strong signal observed for the process,

\[
\text{Br} + \text{HI} \rightarrow \text{HBr}^* + \text{I} \quad \Delta H = -16.2 \text{ kcal/mole}
\]

with the same experimental conditions. In the case of the \( \text{Br}^*(2P_{1/2}) + \text{H}_2\text{S} \) experiments, 470 nm light was used to photodissociate \( \text{Br}_2 \) to give one excited atom and one ground state atom. In this case, \( \text{HBr}(v=1) \) product molecules were observed from the reaction of \( \text{Br}^* \) with \( \text{H}_2\text{S} \). By comparison of the \( \text{HBr}(v=1) \) signal with the \( \text{Br}^* \) emission signal, a preliminary conclusion is that the major quenching channel is the reactive process,

\[
\text{Br}^* + \text{H}_2\text{S} + \text{HBr}(v=1) + \text{HS}(v=0) \quad \Delta E = 0.15 \text{ kcal/mole}
\]

It is expected that the small endothermicity for this process is overcome by the initial translational activation energy in the encounter.

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\[ \text{Br}^* + \text{H}_2\text{S} \]

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**Figure 4.** Possible energy transfer and reactive channels for the \( \text{Br}^*(2P_{1/2}) + \text{H}_2\text{S} \) reaction shown as a function of the energetics required.
Conclusion

We have demonstrated that the technique of laser-initiated chemiluminescence used in these experiments gives valuable information about the channeling of reaction exothermicity into product vibrational energy in atom-diatom and atom-triatom reactions, as well as providing rate data for the various processes. Information concerning the significance of all possible reaction and energy transfer channels has also been ascertained.

Acknowledgment

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References

2. Vibrationally Excited Hydrogen Halides, NBS Special Publication 392 (U.S. Dept. of Commerce) and references therein.