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THERMAL RATE CONSTANTS, ENERGY DEPENDENCE AND ISOTOPE
EFFECT FOR LASER INITIATED HALOGEN-HYDROGEN HALIDE REACTIONS

Chang-Chi Mei
(Ph.D. thesis)

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ABSTRACT

The laser initiated chemical reaction method has been used to determine the thermal reaction rate constants for the reactions $Y + HX \rightarrow HY(v \geq 0) + X$, $Y = Cl$ or Br and $X = Br$ or I , in the temperature range $220 - 400^\circ K$. The Y atoms are produced by Y_2 photolysis. The reaction rates vary slowly with temperature. For $Cl + HI$ the effective cross section reaches a maximum of $31 \text{ \AA}^2$ near $300^\circ K$. For $Cl + HBr$, although no maximum is observed within the limited temperature range, the rate is increasing much less rapidly at high temperature than at low temperature. For $Br + HI$, the cross section decreases slightly with increasing temperature. The dependence of the rate on reagent translational, rotational energy and H-D substitution has been measured for the reaction $Cl + HI$. It is found that a factor of 3.9 increase in translational velocity over room temperature actually decreases the cross section for $Cl + HI$ and DI by a factor of 9 and 6.6, respectively. However, at 13.8 kcal/mole collisional energy, the cross section increases by 1.2 as the rotational temperature increases from 223 to $295^\circ K$. The isotope effect increases in favor of HI from 1.5 to 2.7 as the temperature decreases from 400 to $223^\circ K$. A reaction model is proposed for thermal reaction in which the attacking halogen atom is attracted to the halogen end of the hydrogenhalide and then rotation of the hydrogen completes

the reaction. The reaction at 13.8 kcal/mole translational energy results mostly from head-on collinear encounters of Cl with the H of HI. The isotope effect is thought to be a result of the difference in rotational velocity between HI and DI and perhaps of the existence of a barrier along the rotational coordinate.

Dedication
to my parents

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CHAPTER I

INTRODUCTION

Over the past few years, a wide variety of chemical reactions involving halogens and hydrogenhalides have been extensively studied.¹⁻¹¹ These reactions are of particular importance both for a practical understanding of chemical laser processes⁴ and for a theoretical elucidation⁹⁻¹¹ of elementary three-center exchange reactions. Due to computational limitations,¹² detailed information on the dynamics for this many-particle system cannot be provided by fundamental quantum mechanics. However, with the advent of large, fast digital computers, it is possible to attempt to understand chemical dynamics from the classical motions^{12,13} of the atoms and molecules on semi-empirical potential energy surfaces. Thus, it is essential to draw sufficient macroscopic and microscopic information¹⁴ in detail from experimental data in order to construct an accurate potential energy surface.

The exothermic halogen-hydrogenhalide reactions have been studied in molecular beams^{7,8} and by infrared chemiluminescence.¹ These studies have given the angular distribution of products and the energy distribution of the products quantities which are more sensitive to the potential surface for the products as they separate.¹⁵ A crucial piece of missing information is the shape of the potential surface for the approaching reagents which is the determining factor

for the total reaction rate.³ The purpose of this work is to provide a better understanding of the characteristic features of the entrance valley by investigating the temperature variation of the rate, the energy dependence of the reaction and the relative rates for two competing isotopically substituted reactions.

All of the reaction rates are relatively fast and measured by the laser flash photolysis method.³ This powerful method extends the time resolution down two orders of magnitude from that of standard flash photolysis techniques, allowing the measurement of rates of reactions which occur in just a few gas kinetic collisions. The opportunity to use monoenergetic reactants and the high sensitivity of the method are of considerable general value in the study of many chemical reactions.

This thesis consists of two major parts. Chapter II is a presentation of the experimental apparatus and techniques. In Chapter III, results and discussions are presented along with suggestions for future work. It is hoped that by probing different aspects of the potential energy surface a complete construction of the surface and a deeper understanding of the dynamics of this system will be obtained.

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CHAPTER II

EXPERIMENTAL

A. Introduction

The experimental work performed involves time-resolved infrared fluorescence of the reaction products which are formed by laser-initiated halogen-hydrogenhalide (also DI) reactions.^{1,2} A Molelectron N₂-laser or a CMX-4 dye laser is used to dissociate the halogen molecule and initiate the reactions. The high power, short pulse duration and high repetition rate of the lasers allow the molecular dynamics experiments to be accomplished.

Before a detailed discussion of the specific parts of the experiments, it is helpful to understand how they fit into the total experimental scheme. Figure II-1 shows the overall schematic of the basic experimental arrangement. A flow system is designed to keep constant reagent pressures and to minimize wall-catalyzed prereactions.^{2,3} Gases are mixed before entering the reaction cell and finally pumped through a series of liquid N₂-traps to separate the corrosive condensibles from the Ar buffer gas. Flow rates and total pressures are measured at a constant pumping speed and steady flow. Laser beams are collimated and focused into the cell. The fluorescence is imaged onto an infrared detector.^{4,5} The detector signal is amplified, digitized, signal averaged and eventually plotted on an X-Y recorder. The experimental apparatus and methods are described fully in the following

Figure II-1. Basic experimental schematic. The laser beams are collimated and focused into the gas reaction cell. Fluorescence is collected with a lens and detected by an infrared detector. After amplification, the signal can be averaged and plotted out.

sections. The construction of a new cell for temperatures from 220 to 400°K is described in detail.

B. Gases

Sample preparation is performed on a standard glass vacuum system equipped with a liquid N₂-trap and a mercury diffusion pump. Dupont Krytox grease is used on all high vacuum stopcocks and joints. Ultimate pressure is measured with a Phillips gauge as well as a factory calibrated McLeod gauge, sensitive to $\sim 10^{-6}$ torr. Pressures of 10^{-6} torr are routine throughout the entire line with leak rates less than 2×10^{-6} torr/min.

Gases from Matheson are argon (99.999%), chlorine (99.96%), HBr (99.8%) and HI (98%). High pressure gas cylinders are connected directly to the vacuum line. Gas is introduced through a needle valve with a main shut off valve from Matheson. Needle valves are all made of monel to protect against the corrosive gases. The argon gas is used from the tank without further purification. Each reagent gas is purified by distillation from a freezing slush bath (e.g., hexane or chloroform) at a temperature low enough to produce a few torrs pressure to a 5 - 10 liter reagent bulb with its cold finger at 77°K. In each case only the middle fraction of the distillate is used. Bromine (Mallinckrodt, reagent grade) is purified by repeated freeze-pump-thaw cycles over liquid nitrogen. DI is obtained from Merck, Sharp

and Dohme Co. in 1-liter sealed glass bulbs. Purification is done by degasing at 77°K. The rated purity is 98%. Before using the DI gas, the entire vacuum system and flow system are deuterated by repeatedly filling it with 10-30 torr of DI for 40 - 60 min and pumping down to at least 10^{-3} torr before each refill. The isotopic purity of DI is checked by IR absorption spectroscopy. The peak absorption of the HI contaminant in 50 torr DI is less than 4% that of a blank test containing 50 torr HI. Experiments with HI or DI are performed under red safety lights to prevent photodecomposition.

C. Reaction Cell and Temperature Control

Gas reaction experiments are studied over the temperature range 220°K - 400°K. Condensation of I_2 and Br_2 on the cell windows prevents work at lower temperatures. The reaction cell is constructed with three criteria in mind:

- (i) good mixing among the gases but minimum probability for prereaction;
- (ii) good thermal isolation from the environment and thermal equilibrium within the reaction chamber;
- (iii) optical access to the laser beam as well as good transmission for the desired fluorescence.

Two fluorescence cells are used in these experiments. The first cell is all made of quartz. Quartz windows⁴ provide both optical access to the UV or visible light employed and good transmission for the infrared fluorescence of the

product molecules HCl and HBr. Windows are attached using a glass transfer tape (Vitta Corp., G 1015). Figure II-2 shows a three chambered quartz cell situated in a Dewar which can be filled with coolant or heated oil. The two evacuated cylindrical outer chambers of the cell provide thermal isolation to the reaction chamber. The reaction chamber is 1 inch diameter x 4 inches long. Gases are passed through coils immersed in the Dewar to achieve thermal equilibrium before entering the cell. Each coil is 3.5" - 4.5" long made by winding 3 mm I.D. glass tubing into 1" diameter helices with 1/2" per turn. There are three coils in series in the Ar + Y₂ path and one coil for HX. The HX (X = I, Br) is then injected through six holes (the first set of three is shown in the diagram) directed against the Ar + Y₂ (Y = Cl, Br) flow and mixed ~ 7 mm before they enter the cell. This not only ensures good mixing but also decreases the possibility for prereaction³ since the gas inlet is ~ 15 mm from the observed reaction zone (other important factors concerning prereactions will be discussed later).

A second cell (Figure II-3) very similar to the first one is constructed for the detection of the DCl infrared fluorescence. The major difference between these two cells is the IR windows. In order to have good transmission for the DCl fluorescence, the quartz windows are replaced by a 1 inch diameter x 0.04 inch thick sapphire window (Adolf Meller Co.) and a 2 inch diameter x 6 mm thick KCl window

Figure II-2. Reaction cell for the temperature dependent measurements of the Y ($Y = \text{Cl}, \text{Br}$) + HX ($X = \text{I}, \text{Br}$) experiments. HCl and HBr infrared fluorescence are observed through the quartz windows.

Figure II-3. Reaction cell for temperature dependent measurements of the Cl + DI experiments. DCI infrared fluorescence is observed through the sapphire and KCl windows. The sapphire window is fused onto the Pyrex 7740 glass through graded seals in the series 2954-7052-3320-7740

(Harshaw). The difficulty involved is the sealing procedure for the sapphire window. The thermal expansion coefficient (Table II-1) of sapphire is significantly different from that of quartz, therefore, they can not be fused together. Neither is the transfer tape successful in attaching the window. Thus this cell is mainly made of pyrex and the sapphire window is fused onto it by the Graded Seal method and a very careful preheating of the sapphire. The detailed procedure is as follows (see Footnote):

- (i) prepare a 1 inch diameter tubing with graded glasses in the series 7740-3320-7052-2954 (material properties are listed in Table II-1) and grind the 2954 end;
- (ii) hold glass tubing in lathe and preheat the 2954 glass to softness by torch;
- (iii) hold the sapphire window on Vacuum Chuck in lathe, evenly preheat it to glowing orange (~ 5 min) by an induction heater (125 kHz, 5 kw);
- (iv) move the sapphire window toward the glass tubing, remove the torch as they are very close but leave the induction heater on to keep the sapphire window from cracking by fire;
- (v) bring them into contact and they are fused together.

As designed and executed by Bob Hamilton of the Electronic Engineering glass shop.

TABLE II-1. Thermal Expansion Coefficients of the Materials
Used in the Construction of the Reaction Cell.

Material Name	Expansion Coefficient ($^{\circ}\text{C}^{-1}$)
Quartz	0.5×10^{-6}
Sapphire (0° cut)	6.6×10^{-6}
Thermometer Tubing 2954	6.6×10^{-6}
Kovar Sealing Glass 7052	4.6×10^{-6}
Uranium Glass 3320	4.0×10^{-6}
Pyrex 7740	3.2×10^{-6}

The KCl top window is glued on by 3M HiFlex Epoxy. This epoxy glue is chosen for its high vacuum sealing property, its resistance to acetone and its high flexibility at various temperatures. The front quartz chamber is attached on the pyrex reaction chamber by glass transfer tape. The cell is sealed onto a stainless steel dewar by the 2-212 EPR O-ring. Insulation is achieved by asbestos mud.

Cell temperatures below 295°K are controlled by a cold slush bath (e.g., a dry ice and acetone mixture). High temperatures are controlled by an external, constant temperature circulator (Haake, Model FT). It has a direct temperature dial feature, utilizing a platinum resistance sensor. Dow Corning 550 Silicone oil is circulated as a heat transfer fluid. A calibrated thermistor (Omega Eng. Inc. UUA 32J4), with an epoxy encapsulated thermistor sensor in a screw-mounted aluminum housing with teflon insulated leads, is sealed into the gas flow through a quartz sleeve (Figure II-2) to measure the cell temperature. It is a Resistance-Temperature device with time constant ~ 1 second. The cell temperature is found to be well equilibrated with the external bath temperature. Cold bath temperatures are kept stable and uniform to better than $\pm 1^\circ\text{K}$ throughout the Dewar. High temperatures are stable to $\pm 2^\circ\text{K}$. The Ar partial pressure is 30 - 100 times that of the reagents and served as a thermal buffer.

D. Total Pressure, Flowrate and Partial Pressure Determinations

Total pressures and flowrates are measured under a constant pumping speed and steady flow. A cold finger on each reagent bulb is held at low enough temperature to maintain a constant forepressure of about 200 torr for steady flow. The reagent forepressures are measured with Acco Helicoid K-monel pressure gauges. Total pressures in the cell up to 50 torr are measured with a Pace P7D-1 transducer and Celesko CD-10 carrier demodulator. Calibration against actual pressure is carried out by volume expansion. A precision bore mercury manometer read by a cathetometer served as the primary calibration standard. Linearity of 1% uncertainty is obtained.

The gas flows are regulated by monel needle valves in the otherwise all glass system. In each experiment the gases are flowed for 1 minute to stabilize flows before firing the laser. Flowrate determination is a very important part for these experiments since it contributes the major systematic error in calculating the reagent partial pressures and hence in determining the absolute reaction rate constants. In this work, the flowrates are measured by Hastings-Radist LF-20 electronic flowmeters which give a direct measurement of the mass flow in the range of 0 - 20 Standard CC/min (SCC/min). The calibration is against the increase of the actual pressure within a certain period Δt at fixed flowrate.

The actual flowrates are calculated from Equation (1) below:

$$F_i \left(\frac{\text{SCC}}{\text{min}} \right) = \frac{\Delta P_i (\text{torr})}{\Delta t (\text{sec})} \cdot V_f (\text{CC}) \cdot \frac{60 \left(\frac{\text{sec}}{\text{min}} \right)}{760 \left(\frac{\text{torr}}{\text{min}} \right)} \quad (1)$$

where subscript i stands for the reagent i and V_f is the entire volume of the flow system. A complete diagram of the flow system is shown in Figure II-4. Typical calibration curves for reagent gases are shown in Figure II-5. The reliability of these flowmeters is carefully tested by repeated calibration. A stability of 3% is found over a period ~ 1 week and 6% for ~ 1 month. Nevertheless, the flowmeters are calibrated each time for the different gases before an experiment. Furthermore, the calibration of the electronic flowmeter is independent of the forepressure (100 - 300 torr) of the gas in the storage bulb. This avoids interpolation of the calibration to the actual forepressure.

The HX partial pressure needs to be known for the determination of the rate constants (detailed kinetic scheme is discussed in section B, Chapter III). It can be calculated from the individual flows (F_i) for all components in the gas mixture and the total pressure (P_t) in the reaction cell by $P_i = P_t \cdot (F_i / \sum_j F_j)$, provided that:

- (i) the gases are well-mixed when they reach the reaction cell;
- (ii) the concentration of [HX] (or [DI]) is not reduced by reaction with $\text{Cl}\cdot$ or $\text{Br}\cdot$ atom;
- (iii) the concentration of [HX] (or [DI]) is not reduced by prereaction with Cl_2 or Br_2 molecules.

Figure II-4. Schematic diagram of the flow system. The volume V_f is defined by the shaded area.

Figure II-5. Calibration of the Hastings flowmeters against the actual flowrates for Cl_2 , Br_2 , HI, DI, HBr.

First of all, the gases are uniformly mixed due to the design of the reaction cell. Secondly, the dissociation of the Cl_2 or Br_2 molecule into atoms⁶ is less than 0.4% per shot within the laser illuminated volume. The fractional change of the HX pressure can be expressed by the following equation:

$$\frac{\Delta P_{\text{HX}}}{P_{\text{HX}}} = (0.4\%) \times \frac{2Y}{1Y_2} \times (\text{laser repetition rate}) \times (\text{flow time}) \times \frac{P_{Y_2}}{P_{\text{HX}}} \times \frac{\text{laser illuminated area}}{\pi \cdot (\text{I.D. of the cell}/2)^2}$$

The laser repetition rate is in the range of 20 - 30 pps.

The flow time estimated from the cell length and the gas flow velocity is less than 0.1 sec. The illuminated area is 0.2 - 0.4 cm^2 and the inner diameter of the cell is 22 mm.

Thus, $\Delta P_{\text{HX}}/P_{\text{HX}}$ should be less than 0.2% at $P_{Y_2}/P_{\text{HX}} = 1$ and the concentrations of the reagents are constant if no pre-reaction is involved. In these experiments the prereaction is primarily wall-catalyzed bimolecular reactions: $Y_2 + \text{HX} \rightarrow \text{HY} + \text{XY}$.³ Thus, a high pumping speed is required² to minimize the time for wall-catalyzed reactions and a large $[\text{HX}]/[Y_2]$ ratio² is necessary to minimize the deviation of the $[\text{HX}]$ concentration calculated from the actual concentration. The relative flows $[\text{Ar}] : [Y_2] : [\text{HX}]$ are varied in the range of 100 : 0.3 : 1 to 100 : 3 : 1 for thermal reactions.

Partial pressures are below 0.15 torr for $\text{Cl}_2 + \text{HI}(\text{DI})$ system, below 0.46 torr for $\text{Cl}_2 + \text{HBr}$ system and below 0.41 torr for $\text{Br}_2 + \text{HI}$ system. The total flow is about 300 $\mu\text{mole/sec}$ with

a pressure of 10 torr in the cell. The highest pumping speed is estimated to be 520 cc/sec (or 140 cm/sec in the cell). Experiments are performed over a wide range of relative flows and over a range of a factor of 2 in pumping speed. The measured results (section C, Chapter III) indicate that the prereaction effect is suppressed to a negligible level with the highest pumping speed and low reagent pressures.

E. Light Sources and Photodissociation of Halogen Molecules

Two different laser sources are used to dissociate the halogen molecules into reactive atoms and therefore initiate the chemical reactions in these experiments. Lasers are employed for their high output power, short pulse duration and high repetition rate. The first one is a commercial 1 megawatt nitrogen laser (Molelectron UV 1000) capable of emitting pulses of 10 mJ energy in a 10 nsec pulse width at repetition rate up to 50 pps. The spectral output is a group of narrow lines from 3370.5 Å to 3371.5 Å. The beam shape is rectangular (6 mm x 25 mm) due to the shape of the discharge channel. The divergence is 1 mrad x 7 mrad. The second laser source is a Chromatix Model CMX-4 flash lamp-pumped dye laser which provides continuously tunable radiation in the visible region from 4450 Å - 7000 Å. The output power is 1 - 10 mJ/pulse with 1 µsec pulse duration at repetition rates up to 30 pps. The beam diameter is ~ 3 mm at output window and the half angle divergence is less than 3 mrad. Laser average powers are measured by a Scientech, Model 473 thermopile. The

calibration is 9.60 mW/mV with an accuracy of better than 1%. A Hewlett-Packard PIN photodiode is used to monitor a fraction of the beam to observe the laser pulse shape and duration.

The absorption spectra for Cl_2 and Br_2 ⁶ molecules are shown in Figure II-6. The corresponding transitions are indicated in the diagram. The absorption of Cl_2 proceeds via the $^1\Sigma_0^+ \rightarrow ^1\pi_{1u}$ transition and leads to two ground state $\text{Cl}(^2P_{3/2})$ atoms.⁷ Cl_2 had maximum absorption at the N_2 -laser output wavelength. For experiments involving Cl atom reactions, a rectangular laser beam from the N_2 -laser (at 6 mJ/pulse, 25 pps) is directed vertically along the longer dimension to the cell by reflecting from 3 front surface Al-mirrors and focused to a 0.2 cm^2 cross section by two lenses, one 80 cm focal length glass lens and one 30 cm focal length quartz lens. The arrangement is shown in Figure II-7. Laser power measured at the cell window is about 2.4 mJ/pulse. A reflecting mirror is installed behind the cell rear window (Figure II-7) to double the optical path and hence increase the absorption. It dissociates about 0.4% Cl_2 molecules within the illuminated volume.

The absorption spectrum of Br_2 is resolved into two transitions,⁸ the $^1\Sigma_0^+ \rightarrow ^1\pi_{1u}$ transition and the $^1\Sigma_0^+ \rightarrow ^3\pi_{0+u}$ transition. An approximate potential diagram for Br_2 ⁹ is shown in Figure II-8. In this work a precise measurement for reactions involving ground state $\text{Br}(^2P_{3/2})$ atoms is desired.

Figure II-6. The absorption spectra for Cl_2 and Br_2 molecules in the visible and uv region. Corresponding transitions are indicated.

Figure II-7. Optical path of the laser beam. W_1 , laser output mirror. W_2 , cell front window. M_1 , M_2 , M_3 & M_4 , reflecting mirrors. L_1 , glass lens. L_2 , quartz lens. P_1 and P_2 are two parallel planes.

Figure II-8. Approximate potential diagram for Br_2 .
The excitation step and curve-crossing
dissociation at 5900 Å is shown.

The dissociation of Br_2 into two ground state bromine atoms may proceed via direct excitation into the $^1\Pi_{1u}$ continuum or into the bound levels of the $^3\Pi_{0+u}$ state followed by predissociation or collision-induced dissociation.¹⁰

Initially the experiments were attempted with the 3900 Å output of the N_2 -laser pumped dye laser (DL-300 model) so that only the $^1\Sigma_{0+g} \rightarrow ^1\Pi_{1u}$ transition was pumped. However, the highest laser power obtained at the cell window was only 0.17 mJ/pulse and the fluorescence signal was poor. Then, the 5900 Å output from the CMX-4 dye laser was selected to dissociate the molecule the other way. The photochemical excitation step and inter-state crossing is shown in Figure II-6. This process has been discussed by Leone¹¹ for excitation at 5580 Å (~ 10 kT below the dissociation limit). Almost no Br^* ($^2P_{1/2}$) is obtained at that wavelength and ground state atoms are produced in large yields. With 5900 Å from the CMX-4, the advantages are:

- (i) The laser output power is high (10 mJ/pulse) at the output mirror) and the beam divergence is small as compared to the N_2 -laser pumped dye laser;
- (ii) excitation energy is ~ 14 kT below the dissociation limit of the $^3\Pi_{0+u}$ state and no Br^* ($^2P_{1/2}$) should be produced;
- (iii) excitation is slightly above the intersection point of the $^3\Pi_{0+u}$ and $^1\Pi_{1u}$ states so that the Franck-Condon principle¹² is not violated for inter-state crossing.

The beam can be directed into the cell without reflecting mirrors. A 30 cm focal length, 2" diameter quartz lens is used to focus the beam to a 0.4 cm^2 cross section. The distance from the laser output mirror to the lens is 200 cm and that from the lens to the front cell window is 25 cm. Laser power measured at the cell window is 9.2 mJ/pulse. Optical path is multiplied to three passes by two reflecting mirrors set in front of the cell window and behind the cell rear window, respectively. The dissociation efficiency from this arrangement is expected to be 3 times higher than from the N_2 -laser pumped dye laser. The estimated dissociation is about 0.15% within the illuminated volume.

F. Fluorescence Detection and Amplification

The successful outcome of the kinetic measurement in these experiments is largely due to the very sensitive photoconductive detectors^{4,5} used. Finzi¹³ has described in detail the theory and practical techniques associated with the detectors used in this work. Infrared fluorescence from the excited states of reaction products is detected by the liquid He cooled, high-speed Ge:Hg detector or Ge:Cu detector with 220 nsec and 375 nsec time constant, respectively. Time-resolved infrared signals shorter than one microsecond are observable with the laser and detection system. A cooled (77°K) interference filter and MgF_2 window (4°K) are situated in front of the detector to limit the background

radiation falling on the detector. The noise level is greatly reduced and the detectivity dramatically increased. Broad band interference filters (OCLI, 1 inch diameter and 0.02-0.06 thick) with germanium or silicon substrates are selected to transmit the desired fluorescence and eliminate the scattered laser light. Transmission ranges are 3-5 μ for the HCl, HBr fluorescence and 4.8-8 μ for the DCl fluorescence. The transmission curves for the filters and the fluorescence bands of the products up to the highest populated vibrational levels are shown in Figure II-9. The relative populations of the product vibrational states¹⁴ are shown in Table II-2. The HCl fluorescence will be completely blocked by the 4.8-8 μ filter if there is any contamination of DI by HI during the Cl + DI experiment. Gas filters are sometimes used. Cells filled with gas and placed between the fluorescence cell and focusing lens, served as selective fluorescence filter. In these experiments, a 2" diameter by 2" long filter cell of HBr gas is used to block signals from $v = 1,0$ fluorescence.

Fluorescence from the reaction cell is collected in the direction perpendicular to the laser beam by a 2 inch focal length CaF_2 lens or NaCl lens (2" diameter) and imaged onto the detector (Figure II-1). The detector element is rectangular, 3 mm x 10 mm area. It is aligned parallel to the laser beam along the longer dimension for a more efficient detection of the fluorescence within the illuminated volume. The

Figure II-9. Transmission spectra of the interference filters and the fluorescence bands of HCl, HBr and DCl.

TABLE II-2. Relative Vibrational Populations of the Products^a
for the Reactions $Y + HX \rightarrow HY + X$

Reaction	v					
	1	2	3	4	5	6
Cl + HI	0.22	0.35	1.0	0.74		
Cl + DI	0.08	0.14	0.35	0.73	1.0	0.05
Cl + HBr	1.0	0.4				
Br + HI	0.8	1.0				

a) Reference 14.

improvement with respect to the perpendicular orientation is usually a factor of 3. The lens is mounted on an X-Y-Z stage to facilitate alignment. One-to-one imaging is empirically determined to be optimum.¹⁵

Detectors are operated with the LH0033 buffer pre-amplifier described by Finzi.¹³ The output signals (in the range of microvolts) are amplified by a wide band amplifier (Keithley, Model 104) with a gain of 100. The amplifier consists of three separate amplifiers, two with gains of 10 and one with a gain of 1. A total gain of 100 is obtained by cascading amplifiers. The two amplifiers with gain of 10 are identical, each with a response from 15 Hz to 180 MHz. Noise of each is less than 35 microvolts rms referred to the input; rise time is less than 3 nsec/amplifier and delay time is less than 5 nsec/amplifier. Its very low noise permits amplification of signals as low as the microvolt region. The characteristic time of the fluorescence signal is in the range of 1 kHz to 1 MHz. It never approaches either the low frequency or high frequency cut-off of the electronics and, therefore, the fluorescence signal is never distorted by the frequency bandwidth throughout the experiments.

The observed signal-to-noise ratio for DCl fluorescence is much worse than that for HCl fluorescence for two reasons:

- (i) the number of photons emitted by a 300°K blackbody greatly decreases with wavelength shorter than 5 μ and hence the noise level decreases rapidly below 5 μ ;^{4,5}

- (ii) the radiative lifetime for DCl^{16,17} is about 4 times longer than that for HCl, thus, the number of photons emitted per unit time from the excited state is 4 times less for DCl if the population is the same.

G. Signal Averaging Electronics

The typical signal-to-noise (S/N) ratios are unity or less for low reagent pressures. Fluorescence signals with enhanced S/N ratios are produced with a good reliable signal averaging system composed of a Biomation 8100 transient recorder and a Northern NS-575 signal averager. The Biomation 8100 digitized the signal into 2048 channels at 10 nsec time intervals or longer. The digital data is then transferred in groups of 512, 1024 or 2048 channels into the Northern signal averager. All of the signals are synchronized with a photodiode pulse. The complete time development of the signal is recovered after each laser pulse and added to the previous accumulation. After N shots, the signal has increased N-fold, whereas the random noise increased by $\sqrt{N}$;¹⁸ therefore, the overall S/N ratio increases by $\sqrt{N}$. Typically 500 - 20,000 shots are averaged to produce final S/N ratios ≥ 20 . The fluorescence intensity vs time is plotted on a Hewlett Packard X-Y point plotter (HP 7004). Dual time base can be set on the Biomation 8100 for the study of the fast rise and slow decay of the signal simultaneously. Time scales are calibrated by a single sweep of the pulse generator with frequencies of 1 kHz, 10 kHz, 100 kHz and 1 MHz.

The ultimate averaging capability is limited primarily by averaging time and non-random noise sources. It is found that the N_2 -laser emits R.F. at a frequency of ~ 6.25 MHz which persists for about 1 μ sec. The pick up is in phase from one shot to the next so signal averaging does not improve the S/N ratio to great extent on short time scales. Triggering is always provided by the photodiode to avoid the pickup through the "synchout" of the laser. Electrical isolation of the laser from the detector, mounting, amplifier, transient recorder and averager is essential. All grounds are made through the signal cables between the instruments. All ground leads impedances are as low as possible and all the instruments except for one are connected to the ac line with two prong plugs to eliminate ground loops. The floating BNC of the detector circuit is replaced by a grounded type and the cable connecting the detector to the amplifier is kept as short as possible. All the electronic detection equipment has a different power source than the laser itself. Doors on the laser equipment are well shielded with insulating metal foils to prevent the R.F. pickup from transmitting through the air. With all these efforts, the R.F. problem has been reduced by a factor of 10. For low level input signal, the R.F. pickup is still comparable. It might be possible to eliminate the problem completely by shielding the detector and the electronic equipment or the laser itself with a well grounded metal screen. It was not attempted due to the limited space for the experimental setup. A reasonable

method to obtain measurable fluorescence trace at the initial 1 μ sec is to subtract the R.F. pick up from the fluorescence signal by utilizing the SUB MODE on the Northern. The basic requirement is that the R.F. is time independent. Usually, the R.F. amplitude was equal to the detector noise after 11 averages. The improvement by subtraction decreased the R.F. by a factor of 10. The reliability of this method is frequently checked up from the flatness of the base line after subtraction and is satisfied throughout the experiments.

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CHAPTER III

THERMAL RATE CONSTANTS, ENERGY DEPENDENCE AND ISOTOPE EFFECT
FOR THE HALOGEN-HYDROGENHALIDE REACTIONSA. Introduction

The exothermic reactions of halogen atoms with hydrogen halides have long been a favorite class of reactions for chemical kineticists.¹⁻³ Hydrogen atom transfer between two heavy atoms appears sufficiently simple to encourage attempts at a complete understanding of the dynamics of this class of reactions. Detailed studies of energy distributions among product molecules⁴⁻⁶ have been made and quantitatively interpreted in terms of dynamics on an LEPS potential energy surface.⁷ These distributions have been the subject of many surprisal analyses^{8,9} and the substance of many excellent chemical lasers.¹⁰ Product angular distributions have been observed in crossed molecular beams.^{11,12} The reciprocity between product energy distributions for an exothermic reaction and reagent energy utilization in the reverse endothermic reaction has been demonstrated experimentally.^{13,14} Laser-excited fluorescence measurements of the reaction rates or cross sections¹⁵ have clouded this simple picture of the Cl + HI collision dynamics. The trajectories on the LEPS surface⁷ which so successfully explain the product energy distributions fail to predict the behavior of the reagents. For Cl + HI the magnitude of the rate constants, the deuterium isotope effect and the cross section change for translationally hot atoms are altogether different from those

predicted. The LEPS potential shape correctly describes the release of energy as the hydrogen atom moves toward its new partner in the exit valley but fails to describe the approach of the reactants in the entrance valley. The shape of the potential in the entrance valley and the dynamics of the reagents in this valley must be studied by measurements of reaction rates and cross sections as a function of reagent translational, rotational and vibrational energy.

Measurements of rate constants as a function of temperature are reported here for a series of reactions:

The energy dependence of the cross section at enhanced collision energy, with various rotational energies, is also reported for the reaction $\text{Cl} + \text{HI}(\text{DI})$. Valuable information about the characteristic features of this system is obtained from these results. A qualitative model based on these data is proposed for the dynamics of these reactions.

B. Basic Kinetic Scheme

The intensity of the fluorescence signal is related to the concentration of the excited product HY (Y = Cl, Br) by

$$I_{HY}(t) \propto \sum_{v,J} f(v,J) \times [HY(v,J)] \quad (1)$$

where v is the vibrational quantum number; and J is the rotational quantum number. The factors $f(v,J)$ include the dependence of the optical transition probability on each vibrational-rotational level as well as the nonuniformity of the detection system (filter and detector) as a function of the individual frequencies.

The relevant kinetic equations are given below with typical experimental characteristic time for the different steps. Atoms are produced by laser photolysis of the halogen molecules.

The atoms are produced with excess kinetic energy. For thermal-reaction studies, they are rapidly thermalized by collisions with Ar:

The detailed process of thermalization will be discussed in Section D. Atoms then react,

and the vibrational energy in the product molecule is finally quenched,

where $\text{M} = \text{HX}, \text{Ar}, \text{Y}_2, \text{Y}, \text{HY}$; $k(v,J)$ is the reaction rate constant for the production of a specified (v,J) state of the product and $k_q^M(v,J)$ is the quenching rate constant of that state. The spontaneous decay of the excited state is negligible due to the relatively long radiative lifetime¹⁶ (10 msec - 120 msec). Also, the loss of Y atoms due to recombination or reaction with X atoms¹⁷ is so slow at low concentration (time constant is about 1 sec at $\text{Y}_2 = 1$ Torr with 0.5% dissociation) as to be negligible.

Since only a small fraction of Y_2 molecules is dissociated, the relation $[\text{HX}] \gg [\text{Y}]$ holds and the concentration of the reagent molecule is constant. It is therefore a pseudo first-order reaction. The solution of the differential equation for the population of coupled vibrational levels is worked out in Appendix I. The result for the time-dependent fluorescence intensity is given by

$$I_{\text{HY}}(t) = \sum_{v,J} A_{v,J} \exp[-\sum_M k_q^M(v,J)[\text{M}]t] - B e^{-k[\text{HX}]t} \quad (5)$$

with $k = \sum_{v,J} k(v,J)$.

The amplitudes $A_{v,J}$ and B are functions of $f(v,J)$, $k(v,J)$ and $k_q^M(v,J)$. The condition $I_{\text{HY}}(t=0)=0$ requires $B = \sum_{v,J} A_{v,J}$. The second term on the rhs describes the

rise of the signal and is given by one single exponential, namely by the time constant for the loss of Y atoms. The first term shows that the decay of the signal is a superposition of all the levels populated in HY. The quenching by HY or Y is negligible due to the extremely low concentration of the quencher. The quenching by Ar¹⁸ or Y₂¹⁹ is also negligible due to non-effective collision compared to that by HX.^{18,20} Therefore, the sum over M is reduced to M = HX in Eq. (5) and omitted in the notation thereafter.

Eq. (5) is then used in a logarithmic form,

$$\ln [Q(t) - I_{HY}(t)] = \ln B - k[HX]t \quad (6)$$

with

$$Q(t) = \sum_{v,J} A_{v,J} \exp\{-k_q(v,J)[HX]t\}$$

The total reaction rate constant k can be determined from the slope of the semilogarithmic plot of Eq. (6), provided the concentration of HX is known. The application of Eq. (6) requires the extrapolation of the decay of the signal Q(t) to t=0. This can be easily done if the decay of the signal is dominated by a single exponential.

Eq. (6) can be accurately approximated by simpler forms under special conditions.

- (i) For the reaction Cl + HI(DI), the quenching rate^{18,20,21} is about two orders of magnitude slower than the reaction rate. Thus, by neglecting deactivation it can be shown that

$$I_{HCl}(t) = I_0 \cdot (1 - e^{-k[HI]t}) \quad (7)$$

$$I_0 = B = \sum_{v,J} A_{v,J}$$

- (ii) For the reaction $\text{Cl} + \text{HBr}$, the quenching rate²⁰ is only about 7 times slower than the reaction rate and cannot be neglected. However, in this case most of the chemiluminescence intensity comes from the $v = 1$ level (Table II-2) as detected by Maylotte. This is also confirmed by observing the HCl fluorescence through a cold HCl gas filter which blocks the $v = 1$ fluorescence from reaching the detector. The intensity of HCl ($v > 1$) thus observed is negligible and the signal intensity can be safely approximated by

$$I_{\text{HCl}}(t) = I_0(e^{-k_q(t)[\text{HBr}]t} - e^{-k[\text{HBr}]t}) \quad (8)$$

Here the rotational states are assumed to be thermally distributed.

In both cases, the result is independent of absorptions in the window material and filters and is not affected by nonuniform detection efficiency.

For the $\text{Br} + \text{HI}$ reaction, the $v = 1$ and $v = 2$ vibrational levels of the product HBr molecule are about equally populated (Table II-2). Nevertheless, it is found experimentally that $Q(t)$ can be approximated by one single exponential. The quenching rate determined in this work is about 30 times slower than the reaction rate. Thus, the signal intensity

is approximated by

$$I_{\text{HBr}}(t) = I_0(e^{-k_q[\text{HI}]t} - e^{-k[\text{HI}]t}) \quad (9)$$

C. Thermal Rate Constants

1. Cl + HI

The time dependent intensity from the reaction Cl + HI is shown in Figure III-1. The signal is averaged over typically 500 shots. The progress of the decay^{18,20} is negligible during the rise time and Eq. (7) is applied for the analysis. A semi-log plot of the rise of the signal is included in Figure III-1.

The experimental conditions and measured reaction rate constants as a function of temperature are summarized in Table III-1. In general, for all of the reactions studied, at least 2 independent sets of experiments are carried out for each temperature. Each set contains 5-10 runs corresponding to different combinations of $[\text{Y}_2]$ and $[\text{HX}]$ pressures. A plot of the rate constant vs $[\text{Cl}_2]/[\text{HI}]$ is shown in Figure III-2. The measured rate constants are independent of the $[\text{Cl}_2]/[\text{HI}]$ ratios at the highest pumping speed (520 cc/sec) and low reagent partial pressures. Hence, the influence of the prereaction¹⁵ $\text{Cl}_2 + \text{HI} \rightarrow \text{HCl} + \text{ICl}$ is suppressed to a negligible level. We know of no accurate determination for the rate constant of $\text{Cl}_2 + \text{HI}$, however, it is believed to be quite slow in the gas phase but quite rapid on surfaces.²² Thus, the prereaction effect is larger at lower pumping speed (Section D, Chapter II) and the measured rate constant

Figure III-1. Fluorescence intensity vs time from the reaction $\text{Cl} + \text{HI} \rightarrow \text{HCl} + \text{I}$ (linear scale rhs). A semi-log plot of the rise of the signal is included (logarithmic scale lhs). The time scale is changed from 1 $\mu\text{sec}/\text{div}$ to 1 msec/div at the break in the time scale.

TABLE III-1. Summary of the Experimental Conditions and Results for the Thermal Reaction of
Cl + HI from 221°K to 400°K

T (°K)	P _{Ar}	P _{Cl₂} (torr)	P _{HI}	k ₁ ^H x 10 ¹⁰ (cm ³ mole- cule ⁻¹ sec ⁻¹)	σ ₁ ^{Ha} (Å ²)
400	12.2 - 13.4	0.03 - 0.09	0.03 - 0.08	1.46 ± 0.08	25.2 ± 1.4
345	12.2 - 13.4	0.05 - 0.09	0.04 - 0.11	1.56 ± 0.08	29.0 ± 1.5
294.5	10.4 - 13.4	0.03 - 0.15	0.06 - 0.14	1.55 ± 0.08	31.2 ± 1.6
274.5	10.5 - 10.9	0.04 - 0.10	0.06 - 0.11	1.41 ± 0.06	29.5 ± 1.3
253	10.5 - 10.9	0.04 - 0.09	0.06 - 0.08	1.24 ± 0.05	27.0 ± 1.1
233	10.3 - 11.0	0.03 - 0.12	0.05 - 0.09	1.08 ± 0.05	24.5 ± 1.1
221	10.4 - 11.0	0.03 - 0.11	0.06 - 0.13	1.02 ± 0.04	23.4 ± 1.0

a) $\sigma_1^H \equiv k_1^H / \bar{v}$.

Figure III-2. Thermal rate constant for the reaction $\text{Cl} + \text{HI}$ vs ratio of partial pressure. $\circ$, rate constant at 294.5°K and pumping speed = 520 cc/sec. $\bullet$, rate constant at 294.5°K and pumping speed = 370 cc/sec. $\blacktriangle$, rate constant at 221°K and pumping speed = 520 cc/sec.

decreases as $[\text{Cl}_2]/[\text{HI}]$ ratio increases due to the deviation from the real $[\text{HI}]$ pressure (see Fig. III-2 at pumping speed = 370 cc/sec). The observations are the same over all the temperature range although only the results from two temperatures are shown. The uncertainties in Table III-1 and in all the rate constant tables thereafter are the standard deviation of a single value from the mean of the complete sets of data. Since there are more than 14 values in each set, these cover random and systematic errors. Systematic errors due to the calibration of the flow meter and capacitance manometer should be less than 5%. The room temperature result $(1.55 \pm 0.08) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ agrees well with Bergmann's result¹⁵ of $k_1^{\text{H}}(295^\circ\text{K}) = (1.64_{-0.08}^{+0.06}) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ within the error limits. The reaction cross section σ is obtained from the standard conversion of rate constant: $\sigma = k/\bar{v}$,²³ where $\bar{v} = (8RT/\pi\mu)^{1/2}$ is the average relative velocity; μ is the reduced mass. A graph of $\log k_1^{\text{H}}$ and $\log \sigma_1^{\text{H}}$ vs T^{-1} is shown in Figure III-3. Since the systematic errors are nearly independent of temperature, the error bars show only the random errors.

2. $\text{Cl} + \text{DI}$

The characteristic time dependent behavior of the intensity is similar to that of $\text{Cl} + \text{HI}$. However, the signal amplitude is much less as discussed in Chapter II and typically 4000 shots are averaged. Here again Eq. (7) is applicable. The

Figure III-3. Semi-log plot of thermal rate constant k_1^H and effective cross section σ_1^H , for the reaction $\text{Cl} + \text{HI}$ vs $10^3/T$. -o-, experimental rate constant. -Δ-, cross section. The error bars show standard deviations.

comments for HI about the prereaction effect are also valid for DI. The experimental conditions and measured reaction rate constants as a function of temperature are summarized in Table III-2. The lower limit of $[\text{Cl}_2]$ pressure for the DI reaction is twice that for the HI reaction due to the poorer S/N ratio. A graph of $\log k_1^D$ and $\log \sigma_1^D$ vs T^{-1} is shown in Figure III-4. The room temperature result $(8.6 \pm 0.50) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ agrees with Bergmann's result¹⁵ of $k_1^D(295^\circ\text{K}) = (8.89_{-0.6}^{+1.3}) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$.

3. $\text{Cl} + \text{HBr}$

A plot of the time dependent fluorescence intensity from the reaction $\text{Cl} + \text{HBr}$ is shown in Figure III-5. Typically 2000 shots are averaged. In this case vibrational quenching of HCl during the rise is no longer negligible and Eq. (8) must be used for the analysis. Fig. III-5 indicates that a fast decay of the signal is followed by a slower one. This fast decay arises from the vibrational energy transfer from HCl to HBr:²⁰

The $V \rightarrow T, R$ relaxation²⁴ of HCl is negligible as compared to the fast V-V relaxation. The back reaction is negligible since $k'_q \approx \frac{1}{3}k_q$ ^{18,20} and $[\text{HCl}] \ll [\text{HBr}]$. However, the slow $V \rightarrow T, R$ relaxation of HBr can be seen since the HBr fluorescence is also transmitted by the filter and the radiative transition probability¹⁶ of HBr is only ~ 5 times less than that of HCl.

TABLE III-2. Summary of the Experimental Conditions and Results for the Thermal Reaction of Cl + DI from 223°K to 400°K.

T (°K)	P _{Ar}	P _{Cl} (torr)	P _{DI}	k ₁ ^D × 10 ¹⁰ (cm ³ mole- cule ⁻¹ sec ⁻¹)	σ ₁ ^{Da} (Å ²)
400	12.2 - 15.4	0.08 - 0.14	0.03 - 0.17	0.97 ± 0.05	16.7 ± 0.8
345	12.2 - 15.4	0.09 - 0.17	0.02 - 0.14	1.01 ± 0.05	18.8 ± 1.0
295	12.2 - 15.4	0.09 - 0.18	0.02 - 0.24	0.86 ± 0.05	17.3 ± 0.9
274.5	12.2 - 15.4	0.08 - 0.14	0.03 - 0.17	0.72 ± 0.04	15.1 ± 0.8
240	12.2 - 15.4	0.09 - 0.17	0.03 - 0.17	0.50 ± 0.03	11.2 ± 0.7
223	12.2 - 15.4	0.08 - 0.17	0.04 - 0.23	0.38 ± 0.02	8.7 ± 0.5

a) $\sigma_1^D = k_1^D / \bar{v}$

Figure III-4. Semi-log plot of thermal rate constant k_1^D and effective cross section σ_1^D , for the reaction $\text{Cl} + \text{DI}$ vs $10^3/T$. -o-, experimental rate constant. -Δ-, cross section. The error bars show standard deviations.

Figure III-5. Fluorescence intensity vs time from the reaction $\text{Cl} + \text{HBr} \rightarrow \text{HCl} + \text{Br}$. The open circles show the calculated signal [Eq. (8) & Eq. (10)] using the best computer fitted constants. The dashed and dotted lines refer to a change in the reaction rate constant by plus or minus 10%, respectively. The bars indicate a simultaneous change in the quenching rate constant. The upper and lower end of the bars correspond to a decrease or increase of the quenching rate constant by 10%, respectively.

In HBr only the $v = 1$ state is populated and an HBr gas filter can be used to eliminate the HBr fluorescence. With such a filter only the fast single exponential decay is found which verifies the reliability of Eq. (8). The gas filter is not generally used since it requires a larger distance between the detector and the cell, resulting in a considerable loss in signal amplitude. Therefore the experiments are done without a gas filter. The HBr fluorescence can also be eliminated by a selected interference filter but at the expense of losing the fluorescence signal from the most populated $v = 3$ and 4 levels of HCl (Fig. II-9). Thus this is not recommended either. The fluorescence intensity is then corrected for the contribution of the HBr fluorescence to the signal. This can be done unambiguously since the rate constants for the population and depopulation are either known^{18,20} or can be determined from this experiment. The contribution of the HBr signal can be easily worked out by following the same procedure as in Appendix I. The result is:

$$I_{\text{HBr}}(t) = C \left\{ \left(e^{-k_{V \rightarrow T, R}[M]t} - e^{-k_q[\text{HBr}]t} \right) - \frac{k_q}{k} \left(e^{-k_{V \rightarrow T, R}[M]t} - e^{-k[\text{HBr}]t} \right) \right\} \quad (10)$$

with the assumption that $k_{V \rightarrow T, R}[M] \ll k_q[\text{HBr}]$. The last term of the rhs describes a fast rise in the HBr fluorescence

which reflects the fast rise in the HCl fluorescence, the second term indicates a further slow rise which results from the V-V transfer of HCl to HBr, the first and third term describe the decay of HBr($v = 1$) via V→T,R processes with rate constant $k_{V\rightarrow T,R}$. A computer program is written for an iterative analysis of the total signal. In a first approximation, k and k_q are determined from the signal disregarding any contribution from HBr fluorescence. From the slope and intensity of the signal at $t > 500 \mu\text{sec}$ where the second and last terms in Eq. (10) are nearly zero, $k_{V\rightarrow T,R}[M]$ and the amplitude C , respectively, are determined. $k_{V\rightarrow T,R}[M]$ is found to be an order of magnitude smaller than $k_q(\text{HBr})$ and Eq. (10) is the correct description of the HBr contribution. Then $I_{\text{HBr}}(t)$ can be subtracted from the total intensity to give $I_{\text{HCl}}(t)$ which is then analyzed for its rising and decaying components to give improved values of k and k_q . With the improved values the procedure is repeated. Convergence to better than 2% is reached after 3 or 4 iterations. Convergence is fast because $I_{\text{HBr}}(t)$ constitutes only a small fraction of the overall signal.

Fig. III-5 also gives an example of how accurately the rate constants can be determined from the iteration procedure. Together with the experimental curve we have shown the calculated form of the signal $I_{\text{total}}(t) = I_{\text{HCl}}(t) + I_{\text{HBr}}(t)$ using the best pair of rate constants fitted. In addition the rate constants have been changed deliberately. The

upper and lower curves are calculated from $k' = k(1 \pm 0.1)$ respectively. The bars indicate a simultaneous variation of k_q . The upper and lower end of the bars correspond to $k'_q = k_q(1 \pm 0.1)$ respectively. The value of k_q would have to be changed by about 30% to compensate for a 10% error in k . With such a combination of k' and k'_q the calculated signal would again coincide with the experimental curve up to about 40 μsec but at the expense of a considerable mismatch at longer times.

No systematic variation of the reaction rate constant with $[\text{Cl}_2]/[\text{HBr}]$ ratio has been found for various temperatures and pumping speeds (Figure III-6). The absence of prereaction is expected since the reported rate constant for this process²² is $5 \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ and is negligible compared to the atom-molecule reaction rate. The experimental conditions and measured reaction rate constants as a function of temperature are summarized in Table III-3. A graph of $\log k_2$ and $\log \sigma_2$ vs T^{-1} is shown in Figure III-7. The room temperature result $(8.4 \pm 0.5) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ agrees with Bergmann's result¹⁵ of $k_2(295^\circ\text{K}) = (7.4 \pm 0.7) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ within the error limit.

Figure III-6. Thermal rate constant for the reaction $\text{Cl} + \text{HBr}$ vs ratio of partial pressure. $\circ$, rate constant at 294.5°K and pumping speed = 520 cc/sec. $\bullet$, rate constant at 294.5°K and pumping speed = 390 cc/sec. Δ , rate constant at 218°K and pumping speed = 520 cc/sec.

TABLE III-3. Summary of the Experimental Conditions and Results for the Thermal Reaction of
Cl + HBr from 218°K to 402°K

T (°K)	P _{Ar}	P _{Cl₂} (torr)	P _{HBr}	k ₂ × 10 ¹² (cm ³ mole- cule ⁻¹ sec ⁻¹)	σ ₂ ^a (Å ²)
402	11.7 - 12.2	0.11 - 0.24	0.06 - 0.19	10.10 ± 0.77	1.68 ± 0.13
349	11.7 - 12.2	0.17 - 0.24	0.04 - 0.12	9.42 ± 0.58	1.66 ± 0.10
294.5	10.1 - 15.0	0.07 - 0.37	0.09 - 0.41	8.40 ± 0.50	1.63 ± 0.10
274.5	10.0 - 15.1	0.09 - 0.38	0.10 - 0.45	7.65 ± 0.52	1.54 ± 0.10
243	9.9 - 15.2	0.10 - 0.35	0.10 - 0.46	6.20 ± 0.43	1.31 ± 0.09
230	9.8 - 15.2	0.25 - 0.35	0.28 - 0.36	5.24 ± 0.35	1.15 ± 0.08
218	15.4 - 15.5	0.18 - 0.25	0.20 - 0.41	4.99 ± 0.40	1.12 ± 0.09

a) $\sigma_2 \equiv k_2 / \bar{v}$

Figure III-7. Semi-log plot of the thermal rate constant k_2 and the effective cross section σ_2 , for the reaction $\text{Cl} + \text{HBr}$ vs $10^3/T$. -o-, experimental rate constant. -Δ-, cross section. The error bars show standard deviations.

4. Br + HI

The time dependent intensity from the reaction Br + HI is shown in Figure III-8. The radiative lifetime¹⁶ of HBr is about 5 times longer than for HCl. Therefore, the signal amplitude is less and typically 4000 shots are averaged. It is found that the signal consists of one single exponential decay and one single exponential rise. The contribution of radiation from HI to the fluorescence signal is negligible since the radiative transition probability of HI²⁵ is about two orders of magnitude smaller than for HBr. No fluorescence signal is observed for the transition of Br(²P_{1/2}) → Br(²P_{3/2}) at 3685 cm⁻¹. The production of Br atom in the upper spin-orbit state is proven to be negligible²⁶ and the single exponential rise of the signal is contributed by the reaction of ground state Br atom alone. The amplitude of the signal indicates that the quantum yield of the ground state atom is fairly large, hence, the inter-state crossing^{27,28} is quite efficient. Eq. (9) is applied for the analysis of the data.

The experimental conditions and measured reaction rate constants as a function of temperature are summarized in Table III-4. The prereaction effect is negligible at the highest pumping speed but is substantial at lower pumping speed and high [Br₂]/[HI] ratio (Figure III-9). A graph of log k₃ and log σ₃ vs T⁻¹ is shown in Figure III-10.

Figure III-8. Fluorescence intensity vs time from the reaction $\text{Br} + \text{HI} \rightarrow \text{HBr} + \text{I}$. The signal consists of a single exponential decay and a single exponential rise.

TABLE III-4. Summary of the Experimental Conditions and Results for the Thermal Reaction of Br + HI from 250°K to 374°K.

T (°K)	P _{Ar}	P _{Br₂} (torr)	P _{HI}	k ₃ × 10 ¹¹ (cm ³ mole- cule ⁻¹ sec ⁻¹)	σ ₃ ^a (Å) ²
374	12.3-15.8	0.09-0.36	0.21-0.32	1.16 ± 0.08	2.46 ± 0.17
344	12.3-15.8	0.08-0.35	0.16-0.31	1.12 ± 0.08	2.47 ± 0.17
294	12.3-15.8	0.10-0.36	0.11-0.41	1.09 ± 0.07	2.60 ± 0.18
274	13.1-15.7	0.11-0.36	0.11-0.38	1.10 ± 0.08	2.67 ± 0.18
250	13.1-15.7	0.10-0.36	0.21-0.37	1.11 ± 0.08	2.85 ± 0.20

a) $\sigma_3 = k_3 / \bar{v}$

Figure III-9. Thermal rate constant for the reaction $\text{Br} + \text{HI}$ vs ratio of partial pressure. $\circ$, rate constant at 294°K and pumping speed = 520 cc/sec. $\bullet$, rate constant at 294°K and pumping speed = 392 cc/sec.

Figure III-10. Semi-log plot of thermal rate constant k_3 and effective cross section σ_3 , for the reaction $\text{Br} + \text{HI}$ vs $10^3/T$. -o-, experimental rate constant. -Δ-, cross section. The error bars show standard deviations.

Bergmann and Leone²⁹ have measured the reaction rate of $\text{Br} + \text{HI}$ at 295°K by laser dissociation of Br_2 in the 4700 Å region. Both ground state and electronically excited Br atoms were produced with a 1 : 1 ratio via absorption to the $\text{Br}_2(^3\Pi_{\text{ou}}^+)$ state.³⁰ A double exponential rise of the fluorescence signal was observed. The corresponding rate constants are $k_{\text{fast}} = (1.0 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ and $k_{\text{slow}} = (0.25 \pm 0.10) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. From the measurement of the decay rate for the excited $\text{Br}(^2\text{P}_{1/2})$ ²⁹ and the correlation arguments,^{29,31} k_{slow} was assigned as an upper limit for the reaction rate constant of $\text{Br}(^2\text{P}_{1/2}) + \text{HI}$. In this work, the reaction rate constant for the reaction of ground state $\text{Br}(^2\text{P}_{1/2})$ with HI has been precisely determined to be $(1.09 \pm 0.07) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. The agreement of $k_3(295^\circ\text{K})$ with k_{fast} confirms the argument made by Bergmann and Leone that the reaction $\text{Br}(^2\text{P}_{1/2}) + \text{HI} \rightarrow \text{HBr} + \text{I}(^2\text{P}_{3/2})$ is at least 4 times slower than that of ground state. Houston³² has discussed the possibility that $\text{Br}(^2\text{P}_{1/2}) + \text{HI} \rightarrow \text{HBr} + \text{I}(^2\text{P}_{1/2})$ is a faster reaction.

D. Energy Dependence of the Reaction Rate

1. General Considerations

The laser energy at $\lambda = 3370 \text{ \AA}$ exceeds the dissociation energy²⁷ of Cl_2 by 27.6 kcal/mole and that at $\lambda = 5900 \text{ \AA}$ exceeds the dissociation energy of Br_2 by 2.8 kcal/mole. The Cl atoms are therefore produced with initially 13.8 kcal/mole translational energy and move with a velocity 3.9 times thermal velocity at 295°K. With no Ar buffer gas in the mixture and an excess of HX over Cl_2 , the first collisions of Cl atoms with HX will occur at high kinetic energy. If only a few gas kinetic collisions are required for a reaction, the first reactive collisions will occur at enhanced collision energy. This is the case in the Cl + HI(DI) system. It can be shown that, for example, the reaction cross section at 295°K for Cl + HI(DI) corresponds to 1.4(2.4) gas kinetic collisions²³ from the gas kinetic cross section σ_g in Table III-5 and the $\sigma_g/\sigma_1^{\text{H}}$ (or $\sigma_g/\sigma_1^{\text{D}}$) ratio. In the Cl + HBr system about 23 collisions are required for reaction. The Cl atom will be considerably slowed down before an observable amount of reaction occurs. Thus, the effect of enhanced energy can not be seen for Cl + HBr. The same argument holds for the Br + HI system.

A time dependent rate constant is observed if the reaction can compete with the thermalization of the Cl atom. The rate constant is expressed as¹

TABLE III-5. Gas Kinetic Cross Sections for Various Collision Partners in These Experiments.

Collisions Partners		Van der Waals Radius (Å)		Gas Kinetic Cross Section σ_g^a (Å ²)
A	B	d_A	d_B^c	
Cl	Ar	3.3 ^b	3.4	35.2
	Cl ₂		4.1	43.0
	HI(DI)		4.1	43.0
	HBr		3.4	35.2
Br	Ar	3.4 ^b	3.4	36.3
	Br ₂		4.3	46.6
	HI		4.1	44.2

a) $\sigma_g = \pi d_{AB}^2$, $d_{AB} = \frac{1}{2}(d_A + d_B)$

b) Approximated from HCl and HBr in Reference 23.

c) Reference 23.

$$k(t) = \int_0^{\infty} \sigma(v) \cdot v \cdot g(v, t) \cdot dv \quad (11)$$

where $g(v, t)$ is the velocity distribution function at time t . The variation of the relative velocity with time and the variation of the reactive cross section with velocity give the slope of the $\log I$ vs t curve at any instant and hence $k(t)$. The cross section can be approximated by the form $\sigma(v) = v^{s-1}$ over a limited velocity range. For $s = 0$, the rate constant is independent of time and a semi-log plot of Eq. (7) gives a straight line. For $s < 0$, the rate constant will decrease with increasing v (at $t \rightarrow 0$) and a smaller slope appears at the beginning. For $s > 0$, the rate constant increases with v and the slope is steeper near $t = 0$. A semi-log plot of Eq. (t) will no longer yield a straight line. Thus, the shape of the $\log I(t)$ vs t curve already allows a qualitative classification of the translational velocity dependence of the cross section. In Figure III-11, the curves are plotted for $s = 0.5, 0$ and -0.5 .

2. Data Analysis

Figure III-12 shows a semi-log plot of the signal vs $P_{HI} \cdot t$ for various compositions $[Cl_2] : [HI]$ using Eq. (7). No Ar buffer gas is added. With an excess of Cl_2 over HI, the initial slope changes very soon to a steeper slope and remains constant thereafter. With a decreasing amount of Cl_2 the point where the curve joins the straight line occurs later since fewer Cl_2 molecules are present which can thermalize the atoms in competition with reactive HI collisions.

Figure III-11. Velocity dependence of the reaction cross section $\sigma = \sigma(v)$, and the relationship with the shape of the time resolved signal intensity $I(t)$. $s = 0.5, 0$ and -0.5 .

Figure III-12. Semi-log plot of the signal vs time from the hot atom reaction of $\text{Cl} + \text{HI}$ for various ratios of partial pressures $[\text{Cl}_2] : [\text{HI}]$. The data are taken without Ar as a buffer gas. The increasing deviation, at early times, from the straight line shows the effect of enhanced collision energy.

The timescale for the thermalization process is determined by the average relative energy loss per collision. The energy after elastic collision with energy E and a scattering angle θ is $E'(\theta) = [1 - \frac{2\mu}{M}(1 - \cos \theta)]E$,³³ where μ and M are the reduced mass and total mass of the system, respectively. At small angles, the contribution to the energy loss is not much. At larger angles, the collisions approach hard-sphere behavior. Thus, the hard sphere model is applied to estimate the average energy loss as the differential cross sections are not available for this system. Averaging $\Delta E(\theta)$ over all angles yields the energy loss per collision; $\langle \Delta E \rangle_{\text{coll}} = \frac{2\mu}{M}E$. The collision rate is given by $n\sigma_g v$;²³ that is, the product of density, gas kinetic cross section and average relative velocity. The rate of energy loss is then $dE(t)/dt = -n\sigma_g v \langle \Delta E \rangle_{\text{coll}}$. Therefore,

$$E(t) = E_0 \cdot \left[\frac{1}{2} v_0 \langle \frac{\Delta E}{E} \rangle_{\text{coll}} \cdot \sigma_g \cdot n \cdot t + 1 \right]^{-2} \quad (12)$$

where E_0 and v_0 are the initial collision energy and velocity, respectively. We have assumed a static target gas. The large difference in mass of Cl and HI and the much larger velocity of Cl justifies this approximation. From Eq. (12) the time dependent average velocity of the initially hot Cl atom can be calculated (as shown in Figure III-13) and compared with the results shown in Figure III-12. The curve in Fig. III-13 is drawn on the same timescale as that

Figure III-13. Time dependence of the average velocity for the Cl atom, calculated from Eq. (12) for $[\text{Cl}_2] : [\text{HI}] = 1 : 10$. The initial velocity of the atoms is v_0 ; the mean thermal velocity is v_{thermal} .

in Fig. III-12. The curve $I_0 - I(t)$ reaches the constant slope close to the time when the Cl atoms are thermalized. The characteristic time for thermalization is about 2 μsec at a pressure of 0.5 torr (without Ar buffer gas) and 0.1 μsec at a pressure of 10 torr (with Ar buffer gas).

Now we can be confident that at long times the reaction occurs with both collision partners thermalized while at short times the reaction of Cl at enhanced collision energy can be seen. Thus a direct comparison of the rate constant in the two regimes is possible from a single curve. The analysis of the ratio of the slope yields the ratio of the rate constant for hot and thermalized Cl atoms. The slope at short times should be determined only at small $[\text{Cl}_2]/[\text{HI}]$ ratio so that the thermalization by Cl_2 can not compete with reactive HI collisions. The absolute value for the thermal rate constant is taken from Section C. It should be noticed that during the hot atom reaction the rotational energy and the vibrational energy of HI are Boltzmann distributed at bath temperature T. Figures III-14 and III-15 show the ratio of the rate constant for thermal and hot atom reactions vs $[\text{Cl}_2]/[\text{HI}]$ at $T = 295^\circ\text{K}$ and 223°K , respectively. Figure III-16 shows the ratio of the rate constant vs $[\text{Cl}_2]/[\text{DI}]$ at $T = 295^\circ\text{K}$. Within the experimental error, the ratio of the rate constant can be well determined as the $[\text{Cl}_2]/[\text{HI}]$ ratio approaches zero. The experimental conditions and results for the hot atom

Figure III-14. The ratio of the rate constant for thermal
($T = 295^\circ\text{K}$) and hot atom (collision energy
 $= 13.8 \text{ kcal/mole}$) reactions vs $[\text{Cl}_2]/[\text{HI}]$

Figure III-15. The ratio of the rate constant for thermal
($T = 223^{\circ}\text{K}$) and hot atom (collision energy
 $= 13.8 \text{ kcal/mole}$) reactions vs $[\text{Cl}_2]/[\text{HI}]$

Figure III-16. The ratio of the rate constant for thermal
($T = 295^\circ\text{K}$) and hot atom (collision energy
 $= 13.8 \text{ kcal/mole}$) reactions vs $[\text{Cl}_2]/[\text{DI}]$.

reactions are summarized in Table III-6. The partial pressures of the reagents are less than 0.4 torr. The uncertainties for the reaction rates and cross sections at enhanced collision energy include the standard deviation of the thermal rate constant and that of the ratio of the rate constant. Comparing the reaction cross sections for thermal and hot atom reactions of $\text{Cl} + \text{HI}$, the parameter s in the expression $\sigma = v^{s-1}$ is estimated to be -0.55 ± 0.05 .

3. Practical Problems

Removing Ar as buffer gas enhances the rate of wall-catalyzed prereaction and gives an uncertainty in the determination of the effective partial pressure of HI(DI) in the reaction chamber. However, only the ratio of the rate constant for thermalized and hot Cl atoms is important. Any uncertainty arising from the prereaction is thereby eliminated.

The energy released by the exothermic reaction and the high kinetic energy carried by the Cl atoms may lead to a thermal heating of the gas and prohibit a proper analysis. The characteristic time for the signal rise is 10 μsec or less. On this timescale only the direct conversion of the energy into translation may interfere with the system. It is found that 70% of the exothermicity of the reaction is converted into the vibrational energy of the products and only 17% appears directly as translational energy at

Table III-6. Summary of the Experimental Conditions and Results for the Hot Atom Reactions of Cl + HI and Cl + DI.

	Collision Energy (kcal/mole)	T ^b (°K)	$\frac{k_1}{k_{hot}}$	$k_{hot} \times 10^{10}$ (cm ³ molecule ⁻¹ sec ⁻¹)	σ_{hot}^a (Å ²)	$\frac{\sigma_1}{\sigma_{hot}}$
Cl + HI	13.8	295	2.30±0.10	0.67±0.06	3.4±0.3	9.0±0.5
		223	1.95±0.10	0.53±0.05	2.7±0.2	7.4±0.4
Cl + DI	13.8	295	1.70±0.10	0.51±0.05	2.6±0.3	6.6±0.4

a) $\sigma_{hot} = k_{hot}/v_o$; v_o = initial hot atom velocity.

b) T is the bath temperature and hence the Boltzmann temperature for the vib-rotational degree of freedom of HI (DI).

thermal energies.⁴ The latter percentage increases with increasing collision energy up to 38% at the initial energy of the atoms.⁵ In total at most 35 kcal/mole per dissociated Cl_2 molecule is converted directly into translational energy. The contribution to the heating by the $V \rightarrow T$ relaxation²⁴ which occurs on a much longer timescale is negligible during the reaction. The excess energy ϵ per molecule in the gas is:

$$\epsilon = n_p \cdot \frac{\sigma_{\text{abs}}}{A} \cdot \frac{P_{\text{Cl}_2}}{P_{\text{total}}} \cdot \delta \quad (13)$$

where n_p is the number of photons focused to an area A , σ_{abs} is the absorption cross section³³ of Cl_2 and δ is the energy released per molecule. Under the experimental conditions: $n_p = 8.5 \times 10^{15}$ photons, $A = 0.2 \text{ cm}^2$, $\sigma_{\text{abs}} = 1.0 \times 10^{-19} \text{ cm}^2$, the increase of the temperature in the illuminated volume is about 15°K with $P_{\text{Cl}_2}/P_{\text{total}} = 1/5$. This can be considered as negligible compared to the initial 13.8 kcal/mole translational energy of the atoms which is 15.3 times the thermal kinetic energy at room temperature. However, an increase of temperature by 15°K will increase the reaction cross section by < 1% and < 7% for thermal reactions at 295 and 223°K, respectively. Also, a possible < 5% error could be involved in the average rotational energy distribution of the reagent. A much stronger focusing of the laser should be avoided due to the unacceptable heating of the gases.

E. Isotope Effect

A semi-log plot of the ratio of the rate constants for the reactions $\text{Cl} + \text{HI}$ and DI vs $1/T$ is shown in Figure III-17. The uncertainty for the isotope effect has been calculated from the standard deviation of each rate constant, not including the possible systematic error. This latter error contribution should be nearly the same in both cases and will cancel out in the ratio.

Figure III-17. Semi-log plot of the ratio of rate constants vs $10^3/T$ for the reactions $\text{Cl} + \text{HI}$ and DI .
 -o-, $k_1^{\text{H}}/k_1^{\text{D}}$ vs $10^3/T$. •, $k_{\text{hot}}^{\text{H}}/k_{\text{hot}}^{\text{D}}$ vs rotational temperature $T = 295^\circ\text{K}$. Δ , $k_{\text{hot}}^{\text{H}}/k_{\text{hot}}^{\text{D}}$ vs translational temperature $T = 5400^\circ\text{K}$. The error bars show the sum of the standard deviations from each rate constants.

F. Discussion

Among the halogen-hydrogenhalide reactions reported in this work, only the reaction $\text{Cl} + \text{HI}$ has been extensively studied in its energy dependence and isotope effect in addition to its temperature dependence. In addition there have been many theoretical attempts^{7,35,36} to elucidate this reaction recently. Thus, we are going to discuss the results for $\text{Cl} + \text{HI}$ in detail and to use it as an example for characterizing the dynamic features of these reactions involving the transfer of a H atom between two heavy halogen atoms. The results for the reactions $\text{Cl} + \text{HBr}$ and $\text{Br} + \text{HI}$ will then be discussed and compared with the $\text{Cl} + \text{HI}$ reaction model.

The observed temperature dependence of the reaction rate for $\text{Cl} + \text{HI}$ is very different from the usual Arrhenius form. The effective cross section increases with temperature, passes through a maximum between 295 and 345°K and then decreases as the temperature is increased further, Fig. III-3. No quantitative barrier height may easily be deduced from these data. An approximate activation energy may be derived from the slope of $\log \sigma$ vs $1/T$; it is 0.5 kcal/mole. The isotopically substituted reaction $\text{Cl} + \text{DI}$ shows a similar temperature dependence behavior with the maximum at about 345°K. The isotope effect increases from 1.5 to 2.7 as temperature decreases from 400°K to 223°K and a distinct curvature is observed

in the semi-log plot, Fig. III-17. In work with hot atoms it is shown that a factor of 3.9 increase in translational velocity over room temperature actually decreases the cross section for $\text{Cl} + \text{HI}$ and DI by a factor of 9 and 6.6 (Table III-6), respectively. The simultaneous excitation of translation and rotation in the thermal rate constant experiments contrasts sharply with the excitation of translation alone in the hot atom case. Since the hot atom velocity is much larger than the 400°K velocity, conclusions must be cautiously considered.

From the available data it is now possible to draw some conclusions about the shape of the ClHI potential surface and to propose a qualitative model for some features of the surface and the associated reaction dynamics. Since the spin-orbit splittings of Cl and I are large, 881 and 7600 cm^{-1} respectively, only one potential surface is relevant here. At the highest temperature of this study the population of the excited $\text{Cl}(^2\text{P}_{1/2})$ is 2%. Searches for the production of $\text{I}(^2\text{P}_{1/2})$ have produced negative results.⁶

Parr et al.⁷ have performed three-dimensional classical trajectory calculations for $\text{Cl} + \text{HI}$ using a parameterized LEPS surface. They were able to match the observed product energy state distribution.⁴⁻⁶ However, the calculated cross sections and excitation function showed poor agreement with experiment. A comparison of the experimental values with the calculated results from various theoretical works

is shown in Table III-7. The cross section calculated on the LEPS surface at 300°K is a factor of 5 less than the experimental cross section measured in this work. In fact, it was necessary to use an HCl stretching force constant for the LEPS surface less than that for the diatomic in order to avoid even smaller cross sections. The cross section calculated at 300°K is smaller than that at 12 kcal/mole by 20%. Thus, the energy dependences from experiment and calculation are in opposite directions. The LEPS surface restricts reaction by Cl to a narrow cone of approach toward the H atom about the HI bond axis with a 0.11 kcal/mole energy barrier along the linear configuration. Since the experimental reaction rate is more than half the gas kinetic rate²³ (Table III-5), it is clear that no serious geometric limitation is possible, and thus the LEPS shape is inadequate as a description of the entrance channel for this reaction at thermal energies.

Recently, Bass et al.³⁵ have carried out quasiclassical trajectory calculations for Cl + HI on a semi-empirical potential energy surface with a shallow well for collinear Cl-HI and also another in the ClH-I valle. Most of the product properties are accounted for with the surface used in these calculations. However, the calculated rate constant at 300°K (Table III-7) is 3 times less than the experimental value and the rate increases slightly as the temperature increases from 300°K to 2000°K. Since the

Table III-7. Summary of the experimentally measured and theoretically calculated reaction cross sections for $\text{Cl} + \text{HI}$ ($T = 295^\circ\text{K}$).

	This work	Theoretical calculations		
		Parr ^a et al.	Bass ^b et al.	Kafri ^c et al.
$\sigma_1^{\text{H}}(\text{\AA}^2)$	31.2	6.5	11	-
$\sigma_1^{\text{H}}/\sigma_{\text{hot}}^{\text{H}}$	9.0	0.8^{d}	-	> 1
$\sigma_1^{\text{H}}/\sigma_1^{\text{D}}$	1.8	1.0	-	-

a) Reference 7

b) Reference 35

c) Reference 36

d) Collisional energy = 12 kcal/mole

surface is still largely restricted in direction for reactive collisions and neither of these shallow wells have any discernable effect on the dynamics,³⁵ a significantly different surface is required.

Kafri³⁷ et al. also examined this reaction using Born approximation calculations. This over-simplified potential surface neglected the repulsion between the non-bonded Cl and I atoms and thus eliminated constraints on the direction of approach for reactive collisions. The computations indicate a decrease of the reaction cross section with increasing kinetic energy. The experimental decrease is significantly steeper. A large increase in calculated cross section with HI rotational energy for rotational quantum numbers $J \geq 10$ might be partially caused by crossing the energy threshold for HCl ($v = 4$). The total cross section is predicted to increase with increasing temperature in the range 220°K - 400°K due to this J dependence. The effect could be responsible for the increase in rate observed at lower temperatures. The fact that the experimental cross section decreases for temperatures above 300°K suggests a stronger translational energy dependence than exhibited by the calculations.

The large thermal reaction rate, the decrease in rate with increasing temperature and the hot atom effect can be understood in terms of an attractive force between Cl atoms and HI. A substantial attraction would pull slow Cl atoms

at moderately large impact parameters into reactive distances while fast Cl atoms would speed by. Both Van der Waals attraction and the chemical bonding characteristic of linear trihalogen and bihalide complexes^{37,38} should produce a significant potential basin with the Cl atom near the I rather than the H of HI. There should be no barrier in the translational approach coordinate to the configuration ClIH.

To complete the reaction the H atom must then rotate around to the Cl atom and react. The rotation must be fast compared to translational separation of the reagents and must have sufficient energy to overcome any barrier in that coordinate. Thus for hot Cl atoms the cross section is small on two counts: the attractive potential has much less effect on the trajectory and the translational velocity is much larger and does not allow time for the H atoms to rotate before the Cl departs. The reaction of hot atoms may in fact result from nearly head-on collinear encounters of Cl with the H of HI. By comparing with theoretical calculation,⁷ it is found that $\sigma_{\text{hot}}^{\text{H}}$ calculated on the currently used LEPS surface is about 2 times larger than the experimental value. However, the calculated cross section was largely reduced by using the correct force constant of HCl.³⁹ For the thermal reaction, the ratio of the rotational velocity of the H in HI and the Cl-HI relative velocity is independent of temperature. Because

of the light mass of the rotating H atom compared to the reduced mass for translational motion the H atom moves about five times faster than the Cl relative to the HI. It is tempting to speculate that the increase in reaction rate at lower temperature is the result of a barrier to reaction in the rotational coordinate. This "rotational-barrier" effect has been discussed before in the work of Stolte et al.⁴⁰ for the reaction cross section of $\text{CsF} + \text{K} \rightleftharpoons [\text{CsFK}] \rightarrow \text{Cs} + \text{KF}$.

The temperature dependence of the reaction cross section can be described by Equation (14) below:

$$\sigma_l^H(T) = \sigma_h^H + A \cdot \frac{1}{T^n} \cdot e^{-V_l/RT} \quad (14)$$

where σ_h^H is the head-on collision cross section: $\sigma_h^H \leq \sigma_{\text{hot}}^H$ ($= 3.5 \text{ \AA}^2$), V_l is the rotational barrier, and $1/T^n$ accounts for the decreasing of the reaction cross section with increasing translational energy. The experimental result for Cl + HI reaction can be reproduced within 4% error with $n = 4.8$, $V_l = 2.9 \text{ kcal/mole}$ and $A = 2.7 \times 10^{15} \text{ \AA}^2 \text{ } ^\circ\text{K}^{4.8}$. The n factor obtained is unreasonably high as compared to that in the cross section function from a long range attraction,¹ $\sigma_R \propto 1/T^{2/S}$ ($S > 2$). Besides, the pre-exponential term (A/T^n) at room temperature is $\sim 3600 \text{ \AA}^2$. It is unreasonably large as compared to the gas kinetic collision cross section. However, we are not attempting to clarify all the physical phenomena by this over-simplified

equation. More information should be provided from the temperature dependence of the isotope effect discussed below.

At room temperature the thermal reaction $\text{Cl} + \text{HI}$ is 1.8 times faster than $\text{Cl} + \text{DI}$. Classical trajectory calculations⁷ show no isotope effect for a LEPS surface (Table III-7). The decrease in rotational velocity by $\sqrt{2}$ between HI and DI may account for the isotope effect in the proposed reaction mechanism. However, the ratio of the rotational velocity between HI and DI is independent of temperature and the existence of a rotational-barrier is required to explain the temperature dependence of the isotope effect. Instead of following the detailed classical trajectory calculations, the basic isotope effect can be qualitatively examined from the transition-state theory based on the statistical model. An activated complex is assumed in the reaction path before a H (or D) atom is transferred from one halogen atom to the other. The ratio of the rate constants for the reaction $\text{Cl} + \text{HI}$ and $\text{Cl} + \text{DI}$ can be obtained from the general expression:⁴¹

$$\frac{k_1^{\text{H}}}{k_1^{\text{D}}} = \left[\frac{Q^{\ddagger 3\text{C}-1}_{(\text{H})} \cdot Q^{3\text{C}}_{(\text{DI})}}{Q^{\ddagger 3\text{C}-1}_{(\text{D})} \cdot Q^{3\text{C}}_{(\text{HI})}} \right] \cdot e^{\epsilon_0/RT} \quad (15)$$

where Q and $Q^{\ddagger}$ are the partition functions of the reactant molecules and the activated complex, respectively; ϵ_0 is a

function of the zero-point energies of HI, DI and the complexes involved. Since the ratio of the translational or rotational partition functions is independent of temperature only the ratio of the vibrational partition functions will affect the slope of the semi-log plot of k_1^H/k_1^D vs $1/T$. The general form of the vibrational partition function is $Q_v = 1/(1 - e^{-h\nu/RT})$. For the reactants HI and DI, $h\nu/RT \gg 1$ and $Q_v = 1$ over the temperature range 200 - 400 °K. Thus,

$$\frac{k_1^H}{k_1^D} = A \cdot \left[\left(\prod_{b=1}^2 \frac{1 - e^{-h\nu_{b(D)}^\dagger/RT}}{1 - e^{-h\nu_{b(H)}^\dagger/RT}} \right) \cdot \frac{1 - e^{-h\nu_{s(D)}^\dagger/RT}}{1 - e^{-h\nu_{s(H)}^\dagger/RT}} \right] \cdot e^{\epsilon_0/RT} \quad (15)$$

where A is the temperature independent factor; $\nu_b^\dagger$ and $\nu_s^\dagger$ are the vibrational frequencies for the bending and stretching modes of the complex respectively, and $\epsilon_0 = (h/2) \cdot [(\nu_{HI} - \nu_{DI}) - (\nu_{s(H)} + \sum_{b=1}^2 \nu_{b(H)} - \nu_{s(D)} - \sum_{b=1}^2 \nu_{b(D)})]$. The term in brackets of Ea. (15) varies from

$$\left(\prod_{b=1}^2 \frac{\nu_{b(D)}^\dagger}{\nu_{b(H)}^\dagger} \right) \cdot \left(\frac{\nu_{s(D)}^\dagger}{\nu_{s(H)}^\dagger} \right)$$

at $h\nu \ll RT$ to 1 at $h\nu \gg RT$. In this reaction system, $\nu_{b(D)}^\dagger \approx (1/\sqrt{2})\nu_{b(H)}^\dagger$ since mainly H and D atoms are moving and also $(1/\sqrt{2}) \leq \nu_{s(D)}^\dagger/\nu_{s(H)}^\dagger \leq 1$. Therefore k_1^H/k_1^D increases with decreasing temperature. The extent of the isotope effect depends mainly on the mass, the zero-point energy difference,

the location and the shape of the energy barrier.^{41,42} For any $v_b^\ddagger$ and $v_s^\ddagger$, it can be shown that the isotope effect contributed from the pre-exponential term in Eq. (15) increases by less than 26% as the temperature decreases from 400°K to 223°K. Thus, ϵ_0 is larger than 420 cal/mole (150 cm^{-1}) in the temperature range 300 - 223 °K and the upper limit for the stretching frequency in the complex ClHI is 1300 cm^{-1} . This implies a highly extended H-I bond in the complex and hence a late barrier in the entrance valley.^{42,43} Theoretically, a late and high barrier gives large isotope effect.⁴² However, the product energy distribution calculated on an LEPS potential surface with a late barrier will deviate from the observed distribution to some extent since the product energy state distribution is essentially determined by the position of the barrier and by the fraction of the energy release taking place along the exit valley.^{44,45} Thus Eq. (15) does not provide a complete description of the temperature dependence of the isotope effect.

It is also possible that some quantum-mechanical tunneling⁴² through the barrier in the rotational coordinate, which favors the lighter H atom, is responsible for the large magnitude and slope of the isotope effect. The probability, $k(E)$, of crossing the barrier for a particle of energy E is found by solving Schrodinger's equation for an one-dimensional Eckart potential energy function V ⁴² (Figure III-18).

Figure III-18. Unsymmetrical one-dimensional Eckart potential

$$V = \frac{-Ay}{1-y} - \frac{By}{(1-y)^2} \quad (17)$$

$$y = -\exp(2\pi x/L)$$

where x is the variable dimension and L is a characteristic width of the barrier. F^* (Figure III-18) is the second derivative of the function at its maximum. The parameters A , B and L are related to V_1 , V_2 and F^* in Figure III-18 by

$$A = V_1 - V_2$$

$$B = (V_1^{1/2} + V_2^{1/2})^2$$

$$\frac{L}{2\pi} = \left(\frac{-2}{F^*}\right)^{1/2} \left(\frac{1}{V_1^{1/2}} + \frac{1}{V_2^{1/2}}\right)^{-1}$$

A particle of mass m and energy E approaching the barrier V_1 is characterized by the relations

$$v^* = (1/2\pi)(-F^*/m)^{1/2}$$

$$\alpha_1 = 2\pi V_1/hv^*$$

$$\alpha_2 = 2\pi V_2/hv^*$$

$$\xi = E/V_1$$

The quantum-mechanical transmission probability is

$$k(E) = 1 - \frac{\cosh 2\pi(a-b) + \cosh 2\pi d}{\cosh 2\pi(a+b) + \cosh 2\pi d} \quad (18)$$

$$2\pi a = 2[\alpha_1 \xi]^{1/2} \left(\frac{1}{\alpha_1^{1/2}} + \frac{1}{\alpha_2^{1/2}}\right)^{-1}$$

$$2\pi b = 2[|(1+\xi)\alpha_1 - \alpha_2|]^{1/2} \left(\frac{1}{\alpha_1^{1/2}} + \frac{1}{\alpha_2^{1/2}} \right)^{-1}$$

$$2\pi d = 2[\alpha_1 \alpha_2 - 4\pi^2/16]^{1/2}$$

When d is imaginary, the function $\cosh 2\pi|d|$ in Eq. (18) becomes $\cos 2\pi|d|$. For a Boltzmann distribution of incident particles, the ratio of quantum-mechanical barrier-crossing rate to classical-mechanical barrier-crossing rate is

$$\Gamma = \frac{k_{qu}}{k_{cl}} = \exp(V_1/RT) \int_0^{\infty} k(E) \exp(-E/RT) d(E/RT) \quad (19)$$

Numerical integration with a CDC-7600 high speed computer is carried out for the integral. The isotope effect is determined by k_{qu}^H/k_{qu}^D .

$$\frac{k_{qu}^H}{k_{qu}^D} = \left(\frac{k_{cl}^H}{k_{cl}^D} \right) \cdot \left(\frac{\Gamma^H}{\Gamma^D} \right) \quad (20)$$

By assuming that there is no classical isotope effect, i.e. $k_{cl}^H/k_{cl}^D = 1$, V_1 and F^* are the only variables to be fitted. The temperature dependence of the isotope effect can be reproduced within 5% error with $V_1 = 2.2$ kcal/mole and $F^* = 1.0 \times 10^5$ dyne/cm. The barrier width L is calculated to be $0.83 \text{ \AA}$ which corresponds to a 30 degree rotation of the H atom in crossing the barrier.

The inclusion of a tunneling correction in Eq. (14) gives

$$\sigma_1^H(T) = \sigma_h^H + A \cdot \Gamma^H \cdot \frac{1}{T^n} \cdot e^{-V_1/RT} \quad (21)$$

With V_1 fitted from the isotope effect and Γ obtained from Eq. (19), the n factor can be determined from the experimental reaction cross section and Equation (22) below

$$\log[(\sigma_1^H(T) - \sigma_h^H) \cdot e^{V_1/RT} / \Gamma^H] = \log A + n \log \frac{1}{T} \quad (22)$$

From the slope of the log-log plot, n is found to be 1.4 ± 0.2 which is more reasonable than $n = 4.8$ obtained from Eq. (14) and $A = (8.0 \pm 1.4) \times 10^5 \text{ \AA}^2 \text{ } ^\circ\text{K}^{1.4}$. The A/T^n term at room temperature is $\sim 280 \text{ \AA}^2$. It is comparable to the elastic integral cross section for the near isoelectronic Ar-Xe⁴⁶ ($454 \text{ \AA}^2$) at 1 kcal/mole collisional energy or Cl-Xe⁴⁶ ($394 \text{ \AA}^2$) at 2.5 kcal/mole collisional energy.

Thus a model for the Cl + HI reaction in which the Cl atom is attracted to I and the H atom then rotates to react with Cl before it departs, provides a qualitative understanding of the thermal reaction rate data. A similar mechanism has been proposed by Nazur, Polanyi and Skrlac⁴⁷ as the main route for the formation of the same product from a different starting point, $\text{H} + \text{ICl} \rightarrow \text{HICl} \rightarrow \text{I} + \text{HCl}$. At room temperature, the reaction $\text{H} + \text{ICl}$ exhibits a well-defined "microscopic branching", i.e. the same reaction products are formed in two distinguishable product energy state distributions. The bimodal HCl product energy distribution suggests that 18% of the reaction proceeds by direct attack at the Cl end of ClI and 82% by indirect reaction from the I end.

In Grover's¹² crossed molecular beam experiment of $\text{Cl} + \text{HAt}$ at 6.5 kcal/mole collisional energy, the center-of-mass angular distribution of the product is forward-backward peaked and almost symmetric about 90° . This is evidence that direct pickup may not play an important role in this reaction. On the other hand, the reaction time is shorter than the maximum given by the statistical model, because the distribution of product translational energies is much narrower and has a much smaller average than the results when all accessible product quantum states are equally populated.⁴⁸ Thus, a temporary trapping of the two halogen atoms is implied.

The dependence of reaction cross section on rotational energy alone has been measured for the hot atom reaction of $\text{Cl} + \text{HI}$. It is found that, at 13.8 kcal/mole collision energy, the cross section decreases by 1.2 (Table III-6) as the temperature decreases from 295 to 223°K (a decrease of average rotational velocity by 1.3). The Boltzmann distributions of the HI rotational states at 295 and 223°K are shown in Figure III-19. No quantitative determination of $\sigma(J)$, i.e. the reaction cross section as a function of the rotational quantum state, can be made from the measured rotational effect. It is believed that the ratio of the interaction time to the rotational period and the rotational barrier^{40,48,14} are the determining factors for the characteristic features of $\sigma(J)$. The experimental observations for the reaction

Figure III-19. Boltzmann distributions of the HI rotational states. -o-, $N(J)$ at 295°K. -Δ-, $n(J)$ at 223°K.

$\text{HX}(\text{J}) + \text{Na} \rightarrow \text{H} + \text{NaX}$ ($\text{X} = \text{F}, \text{Cl}$)⁴⁹ and $\text{F} + \text{HCl}(\text{J}) \rightarrow \text{HF} + \text{Cl}$ ¹⁴ were that the cross section $\sigma(\text{J})$ at first diminished (by approximately 50%) as J increased, and then increased by a similar amount as J increased further. There were indications that $\sigma(\text{J})$ levelled-off thereafter. The minimum in $\sigma(\text{J})$ fell at $\text{J} \sim 7$ for $\text{HF}(\text{J}) + \text{Na}$, at $\text{J} \sim 11$ for $\text{HCl}(\text{J}) + \text{Na}$, and at $\text{J} \sim 2$ for $\text{F} + \text{HCl}(\text{J})$. Thus, the larger cross section for $\text{Cl} + \text{HI}$ at 295°K can be accounted for by the increase of the average rotational velocity or more specifically by the larger population of the higher rotational quantum states at that temperature.

The isotope effect is ~ 1.3 (Table III-6) for hot atom reactions. It is attributed to the difference in rotational velocities between HI and DI and is comparable to the rotational effect mentioned above. Apparently, both the rotational effect and isotope effect are less significant at enhanced collision energy than those at thermal energies (Figure III-17). Thus, the argument that the hot atom reaction results mostly from head-on collision is acceptable.

For the reaction $\text{Cl} + \text{HBr}$, the effective cross section increases much less rapidly at high temperature than at low temperature, (Fig. III-7). The approximate activation energy is 0.8 kcal/mole. The reaction cross section is 20 times smaller than that for $\text{Cl} + \text{HI}$. Both Van der Waals attraction and the chemical bonding characteristic proposed in the $\text{Cl} + \text{HI}$ reaction will be weaker for $\text{Cl} + \text{HBr}$. Thus, the effectiveness of collisions of Cl and HBr from the Br -end is largely reduced. For reaction $\text{Br} + \text{HI}$, the cross section

decreases slightly as temperature increases, (Fig. III-10). No activation barrier is observed. The reaction cross section is 12 times smaller than that for $\text{Cl} + \text{HI}$. The Van der Waals attraction will be stronger for $\text{Br} + \text{HI}$ than $\text{Cl} + \text{HI}$ but the chemical bonding will be weaker. The smaller cross section of $\text{Br} + \text{HI}$ suggests that the chemical-type attraction is the major factor in promoting the reaction cross section for $\text{Cl} + \text{HI}$.

It is interesting to compare our results with the cross section and isotope effect for the $\text{F} + \text{HX}(\text{DX})^{50}$ reactions. A comparison for all of the measured $\text{Y} + \text{HX}(\text{DX})$ cross sections is shown in Table III-8. Both the reaction cross section and the isotope effect are much smaller for $\text{F} + \text{HX}$ than for $\text{Cl} + \text{HI}$. The chemical attraction between F and HI should be even stronger than that between Cl and HI . One possible explanation is that the rotational barrier is much higher for the $\text{F} + \text{HI}$ system so that the effectiveness in crossing the barrier is largely reduced. In fact, the cross section and isotope effect for $\text{F} + \text{HI}$ at room temperature are comparable to those for the hot atom reaction reaction of $\text{Cl} + \text{HI}$. Thus, it is reasonable to speculate that the effective collisions occur from the H end of HI for the $\text{F} + \text{HI}$ reaction.

Grover et al.¹² have measured the reaction cross section for $\text{Cl} + \text{HA}^\dagger$ at an initial translational energy of 6.5 kcal/mole; it is $26 \pm 4 \text{ \AA}^2$. The cross section for $\text{Cl} + \text{HI}$ at the same collisional energy may be interpolated from

Table III-8. Reaction cross sections and isotope effects^a at room temperature.

Atom	Molecule	HI	HBr	HCl
F ^b		4.27(1.29)	5.26(1.29)	1.16(1.38)
Cl ^c		31.2(1.80)	1.63(1.50 ^d)	
Br ^c		2.60		

a) Cross section in $\text{\AA}^2$ ($k^{\text{H}}/k^{\text{D}}$).

b) Reference 50.

c) This work.

d) Reference 15.

the velocity dependence of the cross section and a value in the range $4 - 7 \text{ \AA}^2$ is obtained. This is only about 1/3 to 1/7 the value for $\text{Cl} + \text{HAt}$. For $\text{Cl} + \text{HI}$ reaction, the c.m. angular distribution¹¹ at an initial translational energy of 6 kcal/mole displays a sharp forward peak and a broad distribution extending to about 125° . This is qualitatively similar to the forward peak for $\text{Cl} + \text{HAt}$ mentioned before. Unfortunately, 125° is the largest angle for which information is available in the $\text{Cl} + \text{HI}$ reaction and a backward peak similar to that in the $\text{Cl} + \text{HAt}$ reaction might also exist. The large difference in reaction cross sections between $\text{Cl} + \text{HI}$ and $\text{Cl} + \text{HAt}$ may be attributed to a stronger attraction in the latter system.

There is no quantitative information on either the shape of the potential surface or the collision dynamics for the reaction $\text{Cl} + \text{HI}$. Thus the model proposed is plausible but by no means fully proven. More detailed experimental information on both elastic and inelastic scattering cross sections from molecular beams will be very useful. Extensive theoretical work will be required to derive quantitative information about the shape of the potential energy surface.

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APPENDIX I

Kinetic Scheme for Y + HX reaction

To simplify the problem, only the $v = 0, 1, 2$ vibrational levels of the HY product are considered and the rotational states are assumed to be thermally distributed. Solutions for multi-level population can be obtained by the same procedure. The spontaneous decay rate $k_s(v)$ is so slow compared to $k_q^M(v)$ as to be negligible.

$$\frac{\delta[Y]_t}{\delta t} = -k[\text{HX}]t$$

$$k = \sum_v k(v)$$

$$[Y]_t = [Y]_0 e^{-bt}$$

$$b = k[\text{HX}]$$

$$\frac{\delta[\text{HY}(v=2)]_t}{\delta t} = k(2)[\text{HX}][Y]_t - k_q(2)[\text{HY}(v=2)]_t$$

$$k_q(2) = \sum_M k_q^M(2)[M]$$

By substituting the result for $[Y]_t$ time dependent into the differential equation for $\text{HY}(v=2)$, we have

$$\frac{\delta[HY(v=2)]_t}{\delta t} = de^{-bt} - c[HY(v=2)]_t$$

$$c = k_q(2)$$

$$d = k(2)[HX][Y]_0$$

The linear differential equation is solved for a general and specific solution. The condition $[HY] = 0$ at $t = 0$ is used to evaluate the constant.

	general solution		specific solution
$[HY(v=2)]_t =$	ae^{-ct}	$+$	$\frac{d}{c-b} e^{-bt}$

at $t = 0$, $[HY](v=2)] = 0$. thus, $a = \frac{d}{b-c}$.

$$[HY(v=2)]_t = \frac{d}{b-c} (e^{-ct} - e^{-bt})$$

$$\frac{\delta[HY(v=1)]_t}{\delta t} = k(1)[HX][Y]_t + k_q(2)$$

$$\cdot [HY(v=2)]_t - k_q(1)[HY(v=1)]_t$$

$$= ne^{-bt} + c[HY(v=2)]_t - m[HY(v=1)]_t$$

$$n = k(1)[HX][Y]_0$$

$$m = k_q(1)$$

general solution: $[HY(v=1)]_t = he^{-mt}$

specific solution: $[HY(v=1)]_t = e^{-mt} \cdot \int e^{mt}(ge^{-bt} + fe^{-ct}) \delta t$

Total solution:

$$[HY(v=1)]_t = he^{-mt} + \frac{g}{m-b} e^{-bt} + \frac{f}{m-c} e^{-ct}$$

$$f = \frac{dc}{k-c}$$

$$g = f - n$$

at $t = 0$, $[HY(v=1)] = 0$; thus, $h = -\frac{g}{m-b} - \frac{f}{m-c}$

$$[HY(v=1)]_t = \frac{f}{m-c} (e^{-ct} - e^{-mt}) + \frac{g}{m-b} (e^{-bt} - e^{-mt})$$

The total signal intensity for a three-level system can be expressed as

$$\begin{aligned} I_{HY}(t) &= \sum_v k_s(v) \lambda(v) \cdot [HY(v)]_t \\ &= k_s(2) \lambda(2) \cdot [HY(v=2)]_t + k_s(1) \lambda(1) \\ &\quad \cdot [HY(v=1)]_t \\ &= f(2) [HY(v=2)]_t + f(1) [HY(v=1)]_t \end{aligned}$$

$\lambda(v)$ represents the nonuniformity of the detection system vs wavelength. The final result is

$$\begin{aligned} I_{HY}(t) &= [HX][Y]_o \cdot \left\{ \frac{k(2)}{(k[HX] - k_q(2))} \cdot [f(2) \right. \\ &\quad \left. + \frac{f(1)}{k_q(1)}] \cdot e^{-k_q(2)[HX]t} \right. \\ &\quad \left. \left(\frac{k_q(2)}{k_q(2)} - 1 \right) \right\} \end{aligned}$$

$$\begin{aligned}
& + \left[\frac{f(1)k(2)}{(k[\text{HX}] - k_q(2))} \cdot \frac{1}{\left(\frac{k_q(1)}{k_q(2)} - 1 \right)} - \frac{f(1)}{(k[\text{HX}] - k_q(1))} \right. \\
& \cdot \left. \left(k(1) - \frac{k(2)}{\left(\frac{k}{k_q(2)} - 1 \right)} \right) \right] \cdot e^{-k_q(1)[\text{HX}]t} \\
& - \left[\frac{f(2)k(2)}{(k[\text{HX}] - k_q(2))} + \frac{f(1)}{(k[\text{HX}] - k_q(1))} \right. \\
& \cdot \left. \left(k(1) - \frac{f(1)k(2)}{\left(\frac{k}{k_q(2)} - 1 \right)} \right) \right] \cdot e^{-k[\text{HX}]t} \}
\end{aligned}$$

The last exponential term represents the rise of the signal. Since only the total reaction rate constant k is involved, the rise time is always independent of detection nonuniformity vs wavelength and of detailed relaxation model.

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