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# Molecular Beam Studies of Reaction Dynamics

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# MOLECULAR BEAM STUDIES OF REACTION DYNAMICS

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# Molecular Beam Studies of Reaction Dynamics

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## Scope of Project

The major thrust of this research project is to elucidate detailed dynamics of simple elementary reactions that are theoretically important and to unravel the mechanism of complex chemical reactions or photochemical processes that play important roles in many macroscopic processes. Molecular beams of reactants are used to study individual reactive encounters between molecules or to monitor photodissociation events in a collision-free environment. Most of the information is derived from measurement of the product fragment energy, angular, and state distributions. Recent activities are centered on the mechanisms of elementary chemical reactions involving oxygen atoms with unsaturated hydrocarbons, the dynamics of endothermic substitution reactions, the dependence of the chemical reactivity of electronically excited atoms on the alignment of excited orbitals, the primary photochemical processes of polyatomic molecules, intramolecular energy transfer of chemically activated and locally excited molecules, the energetics of free radicals that are important to combustion processes, the infrared-absorption spectra of carbonium ions and hydrated hydronium ions, and bond-selective photodissociation through electric excitation.

## Current Research and Recent Results

### A. Primary Dissociation Processes

1. 3 and 4 Centered Elimination of $H_2$ in the Photodissociation of $C_2H_4$ (Lee). The photodissociation studies of $C_2H_4$ were undertaken to determine whether the $H_2$ was eliminated via a three- or four-centered mechanism. Since the two possible products, acetylene and vinylidene, have heats of formation that differ by 40 kcal/mole, the TOF spectra of the $H_2$ could potentially distinguish them. Isotopic studies of 1,1 $H_2CCD_2$ and 1,2 cis HDCCDH where we detected HD, $H_2$, and $D_2$, however, were necessary to fully explain the molecular elimination mechanism. These TOF spectra showed that both acetylene and vinylidene are formed in the photodissociation; the cross-section for vinylidene formation is approximately 3 times as great as that for acetylene. This work can be compared with the VUV work also done in this group in which the $H_2$ was detected in specific rovibrational states to give a complete picture of the dynamics of the process. Because of secondary dissociation problems, the H atom TOF spectra from ethylene could not be used to determine the H-$CHCH_2$ bond energy. They do, however, suggest that for secondary dissociation to occur, the vinyl radical ($C_2H_3$) must have 20 kcal/mole in internal energy and that the secondary product, $C_2H_2$, is formed in a highly internally excited state. These observations are new and will be useful in understanding the dynamic details of the atomic elimination channel.

2. Definitive Determination of C-H Bond Dissociation Energy of $C_2H_2$ (Lee). The high resolution photodissociation of acetylene was studied on the 35 inch machine by detection of the fast decomposition fragments (H atom). A 193 nm laser is used to excite a pulsed beam of $C_2H_2$ or $C_2H_4$. A mass spectrometric detector, optimized for light mass detection, is orthogonal to both the molecular and laser beams. These experiments yield high resolution TOF spectra because of the large laser-detector distance (39.0 cm), because the detector is perpendicular to the parent beam which reduces background noise, and because the entire product translational energy distribution can be observed at one lab angle. The time-of-flight (TOF) product spectra obtained contain information about the C-H bond energies, the products' internal energy distributions, and the dissociation mechanism.

The H atom TOF spectra collected showed vibrational and electronic structure from the $C_2H$ product. Using known values for vibrational and electronic $C_2H$ transitions it was possible to determine the translational

energy at which the ground state products, $C_2H$ + H, are formed. This gives a HCC-H bond energy of 131.5 ± 0.5 kcal/mole.

3. State Distribution of $H_2$ Products in 193 nm Photodissociation of $C_2H_4$ (Lee). Jet cooled ethylene was photodissociated at 193 nm using an excimer laser, producing $H_2$ product having both internal and kinetic energy. A near-transform limited laser system was used to generate tuneable narrow band VUV radiation in the regions of the Lyman and Werner bands of the $H_2$ molecule. This was used to interrogate the $H_2$ product from ethylene photolysis via (1+1) resonantly enhanced two-photon ionization. The ion signals were mass separated and measured in a Wiley-McLaren type time-of-flight mass spectrometer. A collinear, counterpropagating pump and probe laser arrangement, combined with optimization of ion optical parameters and precise measurement of VUV laser powers using a platinum photodiode, yielded significantly improved signal-to-noise ratios over previous experiments of this type.

The narrow bandwidth of the probe laser allowed for simultaneous measurement of the $H_2$ product rovibrational state distribution and the Doppler lineshape of each product state (yielding a kinetic energy distribution). The product state distribution was analyzed as being bimodal in character and interpreted as indicating two channels for $H_2$ elimination; the first channel being $H_2$ elimination from the excited state leaving the vinylidene radical, while the second is $H_2$ elimination leaving the acetylene molecule. A large amount of rotational energy in the $H_2$ product is attributed to the latter channel.

4. State Distribution of $H_2$ Products From Photodissociation of Allene (Lee). Allene was photolyzed at 193 nm using an excimer laser. Product $H_2$ molecules were interrogated using (1+1) two photon resonance enhanced ionization with VUV radiation in the same manner as discussed above. Product rovibrational state and translational energy distributions were determined (via Doppler profiles of single quantum states). The VADS technique was implemented in order to estimate internal energies in the $C_3H_2$ fragment.

## B. Reaction Dynamics

1. One and Two Electron Transfers in Reactions of Ba Atoms with Chlorine Dioxide (OClO) (Lee). Our earlier studies of the reactions of divalent barium atoms with nitrogen dioxide ($NO_2$) and ozone ($O_3$) indicated the participation of long lived collision intermediates for several channels despite large reaction exothermicities. These complexes resulted from potential energy barriers for second electron transfer in the singly ionic collision intermediate (e.g., $Ba^+NO_2^-$) for formation of doubly ionic ground state $Ba^{2+}O^{2-}$ products. In several cases, however, such as formation of $Ba^+ON^-$ + O from Ba + $NO_2$, a direct reaction without a long lived intermediate was observed because second electron transfer was not involved. We have extended this series of reactions to Ba + OClO. In this case, formation of ground state BaO + ClO requires a second electron transfer, whereas formation of BaCl + $O_2$ does not. However, both channels were observed with comparable cross sections, and both resulted from decay of a long lived $Ba^+ClO_2^-$ intermediate. The large cross section for formation of BaCl + $O_2$, requiring simultaneously breaking two Cl-O bonds and formation of BaCl + $O_2$ within a single collision is unusual when the highly exothermic atom transfer reaction forming BaO + ClO is available. It is another consequence of the divalent nature of barium. Although formation of BaO + ClO would normally be expected to dominate, a substantial barrier for second electron transfer necessary for BaO formation leads to a long $Ba^+ClO_2^-$ lifetime. As a result, the relatively slow concerted BaCl + $O_2$ channel can compete with formation of BaO + ClO. Further analysis of the data will allow us to extract the BaCl:BaO branching ratio as a function of collision energy, providing us with additional insight into the dynamics of the reaction.

2. Rotational-State Resolved Angular Distribution of DH Products in the D + $H_2 \rightarrow$ DH + H reaction (Lee). During the last few years a rigorous comparison between theoretical calculations and experimental results has become possible due to advances in quantum scattering calculations and due to advances in experimental techniques. At this moment a "perfect experiment," measuring the angular distribution of the products, with complete specification of reactant and product states, is called for.

An issue of much controversy over the past few years has been the occurrence of dynamical resonances in the D/H + $H_2$ reaction. By now the results in Valentini's experiment, which showed the occurrence of dynamical resonances, have been negated by Zare's experiments, which do not show any resonances. Recent

calculations by Miller indicate that state-resolved product angular distributions ought to contain small features which can be ascribed to the occurrence of dynamical resonance.

Using a newly constructed crossed molecular beam apparatus we want to measure the angular distribution of state-specific DH products. A beam of D atoms, generated through photolysis of DI, and a pulsed beam of $H_2$ are crossed, and reaction products are detected downstream from the crossing region, using a Doppler-free (2+1) REMPI scheme and a position-sensistive ion detector. By varying the delay between the detection and the D-atom generation, it should be possible to map out the angular distribution of a specific rovibrational DH-product state, allowing for a more detailed comparison with theoretical calculations than any experiment before.

By using a tunable photolysis laser, the D atom velocity and thus, the collision energy can be tuned. We plan to do this experiment, to look for any evidence of dynamical resonances in these reactions.

3. Orbital Alignment Effects and Dynamics in Ba($^1P_1$)-Bromine Chemi-ionization Reactions (Lee). The reaction of barium with halogen molecules represents an important prototypical case for the study of reaction dynamics in divalent systems. Reaction may be initiated with the transfer of one electron via the celebrated "harpoon mechanism", but there exist a range of possible product channels owing to the prescence of the second valence electron on barium and a second electron-accepting halogen atom. The ground state reaction is dominated by the production of ground state, neutral radical pairs BaX and X (X a halogen atom). In addition, there also exist exoergic electronically excited neutral product channels, and a chemi-ion channel: $BaX^+$ and $X^-$. The latter corresponds to the transfer of both valence electrons from barium. At super-thermal collision energies the single-electron-transfer channel yielding $Ba^+$ and $X_2^-$ becomes accessible. These two ion-producing reaction paths may be used to explore the dynamics of the reaction as the system evolves over several electronic potential energy surfaces.

For barium excited to the ($^1P_1$) electronic state, both of these ion channels are accessible in thermal energy collisions. The use of linearly polarized lasers to prepare the electronically excited barium atoms allows for alignment of the excited state orbital with respect to the relative velocity vector, which is itself well-defined under crossed beams conditions. Because the electronic potential energy surfaces possess different symmetries depending on initial orbital alignment, branching into non-adiabatic reaction pathways may be strongly modulated by means of laser polarization. In the case that the symmetries of the electronic wavefunctions are known for relevant states of the collision complex, the dependence of reaction cross section on initial orbital alignment may be used to infer the internuclear geometry at the critical configuration.

## Future Plans

### A. Intramolecular Dynamics and Primary Dissociation Processes

1. Investigation of Energy Flow from High Frequency Modes to Low Frequency Modes in Unimolecular Decomposition (Lee). The relative efficiencies of energy flow among high frequency modes and low frequency modes can be examined if a molecule can be found which contains two weak chemical bonds of comparable bond dissociation energies and one of the dissociating bonds is coupled strongly to high frequency modes and the other to low frequency modes. $CH_3CH_2OH^+$ satisfies these conditions. This molecule has two dissociation channels forming $CH_3CHOH^+$ + H, and $CH_2OH^+$ + $CH_3$. These two channels are competitive removal of either H atom or $CH_3$ radical from the central C atom and require about 20 kcal/mol of energy. If O-H stretching vibration is excited by a direct overtone excitation beyond the dissociation energy level, the branching ratio measured as a function of excitation energy will reveal the nature of energy flow from the high frequency O-H stretching mode. If the energy is indeed first distributed among high frequency modes before flowing into low frequency modes, one would expect a C-H bond rupture to dominate, contrary to the results expected from a statistical theory.

Comparison of the results of this experiment with those of another experiment in which $CH_3CH_2OH^+$ is deposited with the same amount of internal excitation with different initial conditions will be very revealing. We intend to pursue this by selecting the internal energy of $CH_3CH_2OH^+$ by using the ion-electron coincidence technique.

2. The Photochemistry of Methyl Acetylene at 193 nm (Lee). The investigation of reactions, thermochemistry and photochemistry of small hydrocarbon molecules and radicals with high carbon atoms to hydrogen atoms ratio are very important in combustion chemistry. In our recent investigation of the photodissociation of allene at 193 nm, a question arises on the possible facile isomerization of the excited molecule. The question can be answered if we compare the results of the allene experiment with those of another $C_3H_4$ isomer, namely methylacetylene (propyne). If the H atom migration is facile in the electronically excited state, many common features will be detected between these two systems.

3. Primary Dissociation Processes of Fulvene (Lee). In the primary dissociation of benzene, one of the most surprising observations is the existence of a dissociation channel which involves the elimination of $CH_3$. Since only one H atom is attached to each of the C atoms in a benzene molecule, extensive isomerization and H-migration must take place in the isolated hot benzene. One of the isomers of benzene which might be the precurser of $CH_3$ elimination is fulvene, $CH_2=C_5H_4$. It is speculated that when a H atom migrates from cyclic $C_5H_4$ to $CH_2$, then the C-C bond will become a single bond and the excitation energy is sufficient to break a single C-C bond. Whether this conclusion is correct or not depends on the nature of the $C_5H_3$ radical formed. So far, none of the linear or cyclic structure of a conventional structure suggests that $C_5H_3$ stability is sufficient to drive $C_6H_6 \rightarrow CH_3 + C_5H_3$. Direct dissociation studies of fulvene will be very illuminating. If the above mentioned mechanism is correct, $CH_3$ elimination from fulvene should be a very important channel.

4. Intersystem Crossing and Internal Conversions by Picosecond Photoelectron Spectroscopy (Lee). Some of the most important relaxation processes of electronically excited polyatomic molecules are internal conversion and intersystem crossing, in which part or all of the electronic energy is converted into vibrational excitation. Photoelectron spectroscopy is an excellent tool to identify the form of internal energy in polyatomic molecules. A picosecond VUV pump and probe laser system and a fast photoelectron detector will be developed to carry out time resolved studies of internal conversion and intersystem crossing. Aromatic and halogenated aromatic compounds will be the first series of molecules to be investigated.

5. Photodissociation of Propane and Butane (Lee). Because of the lack of absorption in the visible and UV range, photochemistry of saturated hydrocarbons has not been investigated extensively, and it is not very well understood. With the arrival of a high power, high repetition rate fluorine laser (157 nm), it will now become possible to investigate the photodissociation of saturated hydrocarbons. In the photodissociation of propane and butane, in addition to H and $H_2$ elimination, C-C bond rupture, the possibility of elimination of singlet methylene and methane will be investigated.

6. Primary and Secondary Photodissociation of Aromatic and Heterocyclic Compounds (Lee). As part of a continuing effort to understand combustion related chemistry, especially the initiation processes in pyrolysis of coal, photodissociation of naphthalene, and S- and N- containing heterocyclic compounds will be investigated using the technique of photofragmentation translational spectroscopy.

The information on the primary and secondary processes involved in the pyrolysis of S- and N-containing molecules in coal are very important in the abatement of $NO_x$ and $SO_2$ in the combustion of coals.

7. VUV Photochemistry of Small Molecules (Lee). The important photochemical information which is lacking in the range of 157 nm to 193 nm can now be provided with a new high pulsed energy excimer laser and a Raman shifter. A series of atmospherically important molecules, chlorofluorocarbons, $CO_2$, $O_2$, $H_2O$, and $N_2O$ will be investigated using molecular beam photofragmentation translational spectroscopy.

## B. Reaction Dynamics

1. Reaction of Transition Metal Atoms (Lee). The recent development of an apparatus capable of generating seeded supersonic beams of transition metals will open the door to the study of a broad spectrum of reactions of importance in combustion, catalysis, and corrosion. An exciting prospect, for example, is the reaction of transition metals with hydrocarbons. But during the first year of the investigation of the transition metal atoms we will focus our attention on simple molecules such as oxygen and halogen molecules. By studying

the actual molecular events under precisely defined conditions, a microscopic understanding of these important catalytic reactions may be obtained.

In the catalytic reaction of hydrogen halide elimination from alkyl halide by transition metal atoms, the insertion of transition metal atom into C-X bond is thought to be the first step. The second step involves the migration of one of the H atoms to the transition metal and eliminates either an olefin or a hydrogen halide. Whether a hydrogen halide or an olefin will be eliminated depends on which hydrogen atom migrates and on the nature of the transition metal and carbon atom interaction. The detailed mechanistic and dynamic question can now be answered by investigating these reactions under single collisions of crossed-molecular beams. Molecular beam study of the transition metal chemistry has been our dream for many years and the recent development of a molecular beam source of transition metals will allow us to do so.

2. Molecular Beam Studies of $CO + OH \rightarrow CO_2 + H$ (Lee). $CO + OH \rightarrow CO_2 + H$ is an important combustion reaction and extensive investigations have been carried out recently on the rate constant and the potential energy surface. Calculations by Schatz show that both cis- and trans-HOCO are bound by 35 kcal/mol. Observation of gas phase HOCO is recently reported. The crossed molecular beam experiments will be performed on this system for several purposes: (a) to investigate the reaction probability as a function of kinetic energies, (b) to study the dynamics of energy disposal when the products of H atom and $CO_2$ depart, and (c) to prepare the HOCO molecule in the gas phase either through the $HO + (CO)_2 \rightarrow HOCO + CO$ reaction or use CO as a carrier gas in the OH beam source. If the translational energy release is mainly dominated by the exit potential energy barrier, the increased kinetic energy is expected to become internal excitation of the $CO_2$ product.

3. Reaction of Br Atoms with Ozone (Lee). BrO and ClO radical species play a very important role in catalytic destruction cycles of ozone in Stratosphere. The exoergic abstraction reaction $Br + O_3 \rightarrow BrO + O_2$ will be studied using the crossed molecular beams technique. By heating the high density graphite oven to above 1300°C and expanding the mixtures of $Br_2$ molecule and various rare gases through the nozzle of the oven with over 90% $Br_2$ molecules dissociated into Br atoms, a seeded supersonic Br atomic beam has been produced. Depending on the carrier gases selected, the resulting collision energy range can be adjusted from 6 kcal/mole to 20 kcal/mole. With the time-of-flight (TOF) method, the laboratory angular and velocity distributions of the product BrO can be measured with a rotating mass spectrometric detector. The center-of-mass product angular and velocity distributions which can be derived from these experiments should reveal the role of the $BrO_3$ collision intermediate and provide information about the collision dynamics of this reaction.

Early theoretical calculation and chemical kinetics work have suggested that this reaction occurs through a "harpoon" mechanism with electron density transferred from $O_3$ molecule to Br atom, and that the product BrO would be mostly forward scattered with respect to the incident Br beam. With product BrO TOF measurements at different angles and different collision energies, this work will be able to give direct insight into the detailed dynamics of this reaction.

4. Reactions of $CH_3$ with $O_2$ and $O_2(^1\Delta)$ (Lee). One of the most important elementary chemical reactions involved in the combustion is the slow reaction between $CH_3 + O_2$. $CH_3O_2$ reaction intermediate is known to be bound by 15 kcal/mole and there are two possible decay channels for $CH_3OO$ in addition to the reverse reaction forming $CH_3 + O_2$. The formation of $CH_3O + O$ is substantially endothermic and is not likely to be an important product. The exothermic channel, formation of $CH_2O + OH$, involves the isomerization of $CH_3OO$ to $CH_2OOH$ and is also likely to have a potential energy barrier which exceeds the binding energy between $CH_3$ and $O_2$.

Two types of reactions will be investigated. The first one involves the promotion with a high translational energy and the second using electronically excited $O_2(^1\Delta)$ state. The formation of $CH_2O$ and OH will be investigated by the molecular beam method.

5. Reactions Between Two $CH_3$ Radicals (Lee). Formation of $C_2H_5 + H$ from two $CH_3$ is endothermic by 10 kcal/mole. Since the reaction intermediate is stable $C_2H_6$, if statistical theory is applicable to the decay of the energized $C_2H_6$ intermediate, one should be able to understand this reaction well. But, the applicability of statistical theory to the reaction intermediate formed by the two $CH_3$ radicals is questionable. This is because the motion associated with the six H atoms in ethane is a high frequency vibration and might not share internal

energy effectively. The reaction intermediate might decay back to two $CH_3$ even with sufficient collision energy before extensive intramolecular vibrational relaxation takes place.

Careful experimental investigation is needed to understand how two $CH_3$ radicals can be transformed into $C_2H_5$ + H in energetic collisions.

6. Reactions of Vinyl Radicals with $O_2$ and OH (Lee). In acetylene polymerization, H atoms are known to play an important role, and the vinyl radicals formed by the addition of H to $C_2H_2$ are important intermediates.

Reaction mechanism of vinyl radicals with $O_2$ and OH are two important topics which need to be investigated further. Our recent studies of the photodissociation of vinyl bromide has shown that vinyl radicals can be produced efficiently by using 193 nm photons to dissociate vinylbromide in the supersonic expansion.

Reactions involving two radicals are challenging experiments for crossed molecular beam studies. Further improvement of the crossed molecular beam technique will be needed to advance combustion related chemistry involving polyatomic radicals.

7. Detailed Studies of Orbital Alignment and Molecular Orientation in the Electron Transfer Processes (Lee). In the past several years, we have learned a great deal about the dependence of the alignment of excited orbital in chemical reactions and charge transfer processes. But in many cases, we found that further refinements, especially the departure of molecular orientation, is needed when multiple crossings dominate the observed results.

During the past year, we have learned to produce pulses of molecular beams with 5 mm spread in space and irradiate this pulse synchronously with a pulsed laser. By using a linearly polarized laser, it is possible to destroy all those molecules with undesirable orientation of angular momentum. In other words, it is possible to arrange a collision of a diatomic molecule with an atom in such a way that a molecule will be spinning in the plane which contains a relative vector or in the plane perpendicular to the relative velocity vector. Now, if one carries out the alignment of the excited orbital of atoms with respect to the relative velocity vector, one can obtain unprecedented detailed information on reaction dynamics. For example, in the scattering of Ba + $Br_2$, forming $Ba^+$ and $Br_2^-$, the double-alignment experiment will answer all those questions on the relative importance of charge transfer in the incoming leg or the outgoing leg as a function of molecular orientation and of orbital alignment. This level of detailed studies has never been carried out in the past, but has now become possible.

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