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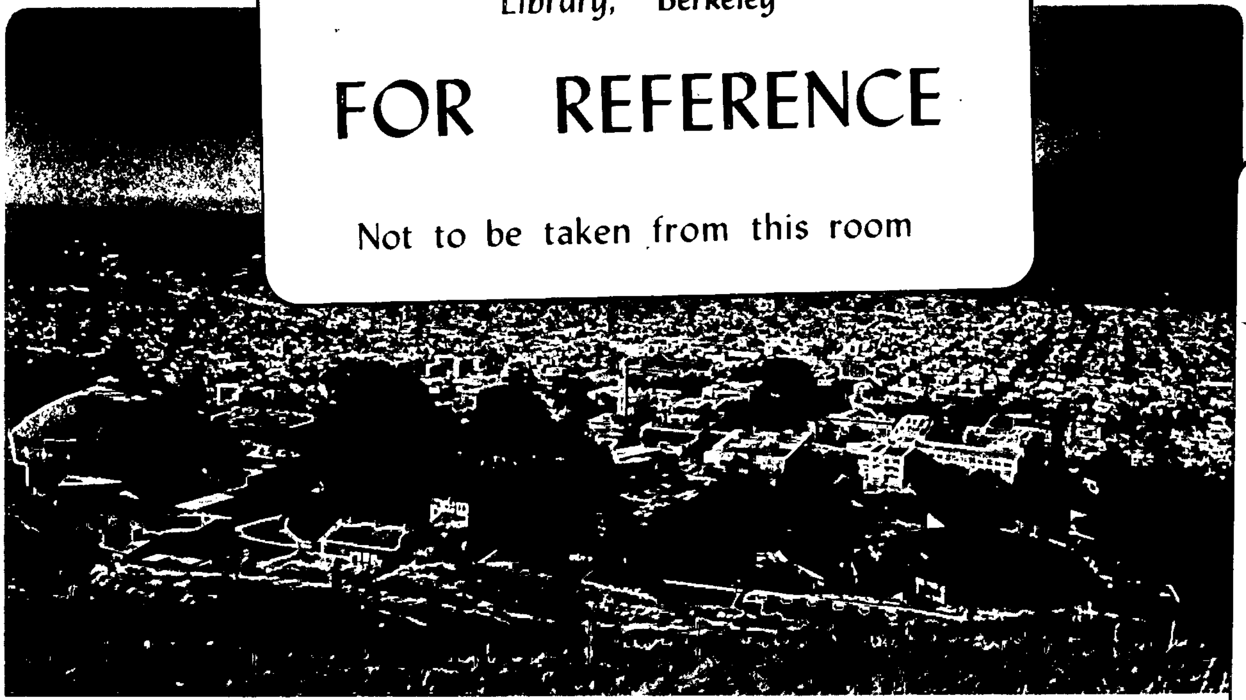

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MOLECULAR BEAM STUDIES OF REACTION DYNAMICS

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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. Infrared Spectroscopy of Ionic Clusters Containing CH_5^+. Ionic clusters containing CH_5^+ have been investigated using infrared laser spectroscopy based upon vibrational predissociation. In this technique, mass-selected parent ions are exposed to tunable IR laser radiation while they are trapped in an octapole ion trap. The number of daughter ions formed by vibrational predissociation of the trapped parent ions is measured with a quadrupole mass spectrometer. This technique has higher sensitivity than direct absorption IR techniques, which is very important for the study of weakly bound clusters which can not be generated in large numbers in the cold ion form.

Last year we studied three solvated CH_5^+ dimers: $CH_5^+(H_2)$, $CH_5^+(CH_4)$, and $CH_5^+(H_2O)$ in the frequency region from 2650 cm^{-1} to 4150 cm^{-1} with 0.2 cm^{-1} resolution. In their spectra, it was found that each band has a splitted feature which may originate from tunneling motion of these clusters. Usually, for weakly bound clusters, there has been observed such a tunneling splitting in their spectra.

2. The Photochemistry of Methyl Acetylene at 193 nm. 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. Photodissociation of CH_3 Radical at 193 nm. There has been recent interest in whether or not the dissociation of methyl radical proceeds via the loss of atomic or molecular hydrogen. Although both channels are thermodynamically accessible at 193 nm, calculations have shown that the "least motion" pathway to H_2 elimination (symmetry forbidden dissociation along the C_{2v} axis) involves a barrier of ~75 kcal/mol. H_2 elimination was therefore thought to be unlikely. More recent calculations have shown that if the H_2 takes a

symmetry allowed "non-least motion" pathway the barrier may be less than 4 kcal/mol. Because there are many such low barrier pathways it is important to study the dissociation of CH_3 and determine the relative importance of both channels.

Preliminary results indicate that at 193 nm CH_3 dissociates to predominately CH_2 + H. The high degree of energy release into product translation is suggestive of dissociation from an electronically excited state. Further work is needed to fully characterize the energetics of the dissociation and understand why elimination of H_2 is not an important process.

4. Molecular Beam Studies of the Retro-Diels-Alder Decomposition of Tetralin. Tetralin (1,2,3,4-tetrahydronaphthalene, $C_{10}H_{12}$) has a hydroaromatic structure typically found in coal and serves as a model coal compound. It has further importance in coal chemistry since it is used as a solvent and a hydrogen donor in coal liquefaction. In these contexts, the decomposition mechanism of this compound is of central importance. Since one its major decomposition pathways involves the retro-Diels-Alder reaction, tetralin also provides an opportunity to investigate the nature of the transition state in this reaction, which has been a source of considerable controversy. The argument has focused on whether the reaction proceeds in a concerted fashion or step-wise, through a biradical transition state. By measuring the distribution of the energy released into translation of the products, one can distinguish these two mechanisms.

Tetralin decomposition was studied using crossed laser-molecular beams techniques. Both ultraviolet (193 nm) and infrared multiphoton excitation were used in conjunction with photofragmentation translational spectroscopy. After 193 nm excitation, tetralin decomposed via the retro-Diels-Alder reaction ($C_{10}H_{12} \rightarrow C_8H_8 + C_2H_4$) and through molecular elimination of H_2. The secondary decomposition of the C_8H_8 product of the retro-Diels-Alder reaction formed C_6H_4 and C_2H_4. The infrared multiphoton dissociation of tetralin also led to decomposition via the retro-diels-Alder reaction. For the retro-Diels-Alder decomposition of tetralin, the measured translational energy distribution of the products was peaked away from zero, indicative of a concerted mechanism. This indication was supported by using impulsive models of the partitioning of energy into the translational degrees of freedom.

B. Reaction Dynamics

1. $D + H_2 \rightarrow DH + H$ High Resolution Reactive Scattering Experiment. We have recently completed constructing and optimizing a new crossed molecular beam apparatus for measurement of rotational-state-resolved angular distributions. A beam of D atoms is generated by laser photolysis of DI and crossed with a pulsed beam of H_2. The DH reaction products are state-specifically ionized downstream from the crossing region using a doppler-free 2+1 REMPI scheme and the resulting ions are imaged onto a position sensitive detector. By varying the delay between the D-atom generation and the detection, we can map out the angular distribution of a specific rovibrational DH product state.

2. Ozone Reactions with Br, Cl Atoms. BrO and ClO radical species play a very important role in catalytic destruction cycles of ozone in Stratosphere. Two elementary reactions Br + O_3 and Cl + O_3 have been studied by crossed molecular beams technique.

(a) $Br + O_3 \rightarrow BrO + O_2$ ($\Delta H^\circ = -30.8$ kcal/mole) has been investigated at five different collision energies from 5 kcal/mole to 26 kcal/mole. BrO product angular distribution and TOF distribution have been measured at each collision energy. BrO_3 collision long-lived complex is evident from BrO angular distribution, even at the highest collision energy. Some forward scattered product BrO (with respect to Br beam) is also observed. Preliminary analysis of the experimental results shows that average translational energy release in the products is about 30% of total available energy.

(b) $Cl + O_3 \rightarrow ClO + O_2$ ($\Delta H^\circ = -39.0$ kcal/mole) has been studied at four different collision energies from 6 kcal/mole to 30 kcal/mole. The results are quite similar to those of Br + O_3, except that there is more forward scattered product ClO, average translational energy release in the products is about 40% of total energy.

Future Plans

A. Primary Dissociation Processes

1. Photodissociation of Propane and Butane. Experiments dating back to the early 1960's have involved probing the dissociation pathways of saturated hydrocarbons. However, to date no agreement has been reached among experimentalists as to the primary processes involved in the dissociation of these simple molecules. During the past year, the primary and secondary processes involved in the 157 nm photodissociation of cyclopropane, propane, butane, and isobutane have been determined. This work was accomplished due in part to the recent availability of a 157 nm high power pulsed vacuum ultraviolet laser. We find H and H_2 loss to be the dominant elimination channels for the straight chain hydrocarbons, butane and propane. In contrast, for the branched hydrocarbon system isobutane, carbon-carbon cleavage is the dominant channel. In the cyclic hydrocarbon, cyclopropane, molecular elimination to form methylene and ethylene is the dominant dissociation pathway.

2. Primary and Secondary Photodissociation of Aromatic and Heterocyclic Compounds. 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.

3. VUV Photochemistry of Small Molecules. Using a new high power VUV excimer laser operating at 157 nm, the photochemistry of CO_2, SO_2, SiH_4, CH_3Cl, CH_3Br and CH_2BrCl was studied via the photofragmentation translational spectroscopy technique.

In CO_2 photolysis an interesting spin-forbidden process was observed, leading to CO + $O(^3P)$ products. The electronic branching ratio $O(^3P)/O(^1D)$ was found to be 0.06. The vibrational branching ratio for the CO(v) + $O(^1D)$ was found to be $[CO(v=0)]/[CO(v=1)] = 1.3$. In the photolysis of SO_2, a channel leading to S + O_2 products was observed, as well as the expected SO + O channel. The molecules CH_3X (X= Br, Cl) were shown to eliminate H, X and HX upon irradiation at 157nm. In addition, the molecule CH_2BrCl was found to eliminate molecular BrCl.

The photochemistry of SiH_4 is interesting and relevant to the microelectronics industry (i.e. laser chemical vapor deposition of silicon thin films). It was previously thought that SiH_4 decomposes through H atom elimination to form the SiH_3 radical. We have shown, however, that molecular H_2 elimination, forming the $SiH_2(^1A_1)$ diradical is a major channel, thus altering our view of silane photochemistry.

4. Photodissociation Dynamics of ClO_2. The photochemical decomposition of the symmetric chlorine dioxide radical (ClO_2) in the atmosphere is of potential importance in the balance of global ozone. However, there has been considerable uncertainty regarding the excited state dynamics of this molecule. Two chemically distinct photodissociation pathways are thermodynamically possible upon electronic excitation at wavelengths shorter than 496nm:

$$OClO \rightarrow ClO(^2\Pi) + O(^3P) \tag{1}$$

$$\rightarrow Cl(^2P) + O_2(^3\Sigma^-_g, {}^1\Delta_g) \tag{2}$$

Although it has generally been believed that channel (1) dominates, there has been considerable controversy regarding the possible existence of channel (2) since it leads to catalytic decomposition of ozone in the atmosphere. Although a number of groups have attempted to determine Cl atom quantum yields and identify the electronic state(s) of the O_2 molecule, the results have been largely inconclusive. We have studied the dynamics of these processes using photofragment translational energy spectroscopy with a tunable excitation laser and have clearly observed both fragment partners for both channels.

5. Primary Dissociation Processes of Fulvene. 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 conventional structure suggests 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.

B. Reaction Dynamics

1. Reactions of Vinyl Radicals with O_2 and OH. 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.

The 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.

2. Crossed Beam Chemistry of Transition Metals with Simple Molecules. 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 to 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.

3. The Reaction of $Li + H_2 \rightarrow LiH + H \quad \Delta E = 192.6$ kj/mol. $Li + H_2$ is a relatively simple system that accurate theoretical prediction of its dynamic behavior might be feasible. With our crossed molecular beam apparatus, this reaction can be studied under single collision condition and the detailed reaction dynamics can be probed. However, in our experiment the ground state lithium atom does not have enough energy to initiate the reaction. Laser excitation of lithium to 2P or 3D states would provide the energy required. The hyperfine structures of lithium electronic state post considerable difficulties in the laser excitation practice. Recently, an optical pumping scheme has been designed, which utilizes two dye lasers to pump lithium to the high-lying states. Experimental results will be compared with theoretical calculations to achieve a better understanding of the reaction dynamics.

4. Reaction of O_3 with unsaturated hydrocarbons. Adducts formed by the addition of O atoms with unsaturated hydrocarbons are important reaction intermediates in the reaction of oxygen atoms with unsaturated hydrocarbons. Just like other radical species, the heat of formation of the adducts is not well determined because of obvious experimental difficulties.

One possible way of obtaining this information is the investigation of the threshold energies required for the formation of adducts in the endothermic reactions between unsaturated hydrocarbons with O_3

$$C_2H_4 + O_3 \dashrightarrow C_2H_4O\bullet + O_2$$

$$C_6H_6 + O_3 \dashrightarrow C_6H_6O\bullet + O_2$$

Molecule-molecule reactions under single collision conditions have only been observed in the reactions of F_2 molecules with iodine containing molecules and benzene. The transfer of an oxygen atom from O_3 to a stable molecules is a very interesting and challenging reaction which is worth pursuing in earnest.

5. Cl Atom Reaction with NO_2 Molecule. Endothermic reaction $Cl + NO_2 \rightarrow ClO + NO$ ($\Delta H^\circ \approx 9$ kcal/mole) is the reaction to connect NO_x and ClO_x groups in atmospheric chemistry. Because $ClNO_2$ is a stable molecule, collision long-lived complex is expected to form in this reaction. By the unique feature of crossed molecular beam experiment, collision energies could be adjusted to probe the energy dependence of reaction probability in this endothermic reaction. Threshold region could be well studied by lowing collision energy.

6. Reaction of Oxygen Atom with Halogen Containing Olefins. Combustion of halogen containing organic molecules, especially the identity of halogen containing products, has been of great interest due to environmental concerns. Reaction of oxygen atoms and halogen containing unsaturated hydrocarbons will be investigated systematically.

For carrying our these investigations, as well as other reactions which are of importance to combustion, a hydrocarbon free molecular beam apparatus is needed. The recent advances of turbomolecular pumps, especially the magnetically suspended turbomolecular pump will make it possible to do so.

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