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KINETICS OF ELEMENTARY ATOM AND RADICAL REACTIONS

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During the past fiscal year we have worked on four projects supported by DOE. These are: (i) the branching ratio for abstraction vs. exchange in the reaction $D+HCl$; (ii) kinetics of $O+H_2$; (iii) energy storage in polyatomic molecules; and (iv) optoacoustic measurements of ir absorption and relaxation in large molecules. The progress in each of these areas, and a brief discussion of future work, is presented below.

A. Abstraction vs. Exchange in $D + HCl$.

The gas phase reaction of isotopically labeled hydrogen atoms with hydrogen chloride molecules can have two possible outcomes: hydrogen atom abstraction to release Cl ,

and chlorine atom exchange to release H ,

The branching ratio, k_e/k_a , has been the subject of controversy for many years.^{1,2} Various experimental studies have yielded values ranging from approximately unity³⁻⁵ to less than 1%.^{6,7} Several studies have indicated that both the activation energy and the steric factor for exchange are much smaller than for abstraction.³⁻⁵ Semi-empirical potential surface calculations¹ and molecular beam data⁸, on the other hand, have indicated that the steric factor for exchange is close to unity. Most recently, several ab initio calculations indicated that there is a large barrier of approximately 20 kcal/mole in the exchange channel.⁹⁻¹¹

Since all previous kinetics measurements of the branching ratio were carried out in either static cells or flow tubes, it appears that the chief source of experimental error has been surface catalyzed scrambling of isotopes. In order to measure k_e/k_a unambiguously, we employed the real time method of flash photolysis with resonance fluorescence detection of atoms. This approach has proved itself to be reliable in our previous work on hydrogen-halogen reactions.¹² The chief experimental difficulty here is to generate D atoms in the presence of HCl without simultaneously producing H atoms. Simply photolyzing a compound such as DI with soft UV radiation is insufficient because DI itself reacts with D atoms much faster than does HCl. The way we solved this problem is to use a mildly focused CO₂ laser to dissociate SF₆ in the presence of an excess of D₂. The reaction F+D₂ produced the required D atoms without producing any detectable concentration of H. The procedure was then repeated with both D₂ and HCl present, while the fluorescence from D, H and Cl atoms were monitored in real time. The result of this experiment is illustrated in Fig. 1. Although large quantities of D and Cl were readily observed, little or no H atoms were detectable. From this experiment we place a conservative upper bound on the branching ratio of $k_e/k_a < 0.002$ at 325 K. Our finding supports the ab initio calculations, and contradicts the semi-empirical studies and the early photochemical experiments.

We plan to extend this work in three ways. First, it is desirable to develop a cleaner source of D atoms. One way to do

Figure 1. Typical fluorescence signal produced with Cl, D, and H atomic resonance lamps. A total gas pressure of 20 Torr was used. The Cl, D, and H signals were accumulated over 30, 100, and 120 flashes, respectively, and then scaled with reference to the total D signal. The residual background due to light scattering has been subtracted from each fluorescent signal. Note the break from semilog to Cartesian coordinates at 50 counts/channel.

this is to use an intense UV laser to dissociate very low pressures of DI. If the ratio of DI to HCl is less than 10^{-3} , the reaction of DI with D can be neglected, or at least accounted for. A second direction is to raise the temperature of the cell in order to measure the Arrhenius parameters of the exchange reaction. We have built for this purpose a quartz cell capable of reaching 1000 K. Third, it would be interesting to study $D+HBr$, for which similar contradictions exist in the literature.

B. Kinetics of $O + H_2$

The reaction of $O + H_2$ is of fundamental importance in combustion chemistry. It is currently the subject of intensive theoretical investigation by Wagner, Bowman, Schatz, and coworkers.¹³⁻¹⁵ The objectives of their work are (i) to develop an accurate potential energy surface for this reaction and (ii) to find reliable and inexpensive methods of predicting the dynamics on that surface. So far several qualitatively different potential energy surfaces have been developed which are consistent with known thermal rate constants. In order to determine which surface is most accurate, it is essential to have more refined kinetic data. A particular example is the effect of isotopic substitution on the reaction rate. For hydrogenic reactions such data should provide a sensitive test for discriminating between different surface features.

Our work on this problem has been along two lines of investigation. First, we are measuring the temperature dependent

rate constants k_{H_2} , k_{D_2} and k_{HD} for the reactions $O + H_2$, $O + D_2$, and $O + HD$, respectively. Although k_{H_2} has been measured extensively, the D_2 reaction has been previously studied only briefly, while the HD reaction has never been reported. We are using the technique of flash photolysis with resonance fluorescence detection of oxygen atoms to measure these rate constants. Although the apparatus is essentially the same as that used in the $D+HCl$ experiment, it has required extensive reconditioning after completion of the halogen study. This has been done, and the $O+H_2$ measurements are in progress.

The second objective is to measure the branching ratio in the HD reaction; i.e.

The technique we have chosen is to measure simultaneously the OH and OD spectra by means of laser-induced fluorescence (LIF).

The relation between the $[OH]/[OD]$ concentration ratio and the spectral peak heights can be determined by first measuring the LIF spectrum for O reacting with a mixture of H_2 and D_2 .

In this case the product ratio is given by:

$$[OH]/[OD] = ([H_2]/[D_2])k_{H_2}/k_{D_2}.$$

Since k_{H_2} and k_{D_2} are being measured independently in the real time flash photolysis experiment, the known product ratio can be used to provide the desired calibration. Finally, since

$k_1 + k_2 = k_{HD}$, the individual rate constants k_1 and k_2 can also be determined.

To perform this experiment we have purchased an excimer-pumped dye laser from Lambda Physics. The laser has been set up, and the requisite 310 nm emission has been obtained by doubling the output from Rhodamine B. We are currently building an apparatus to study the OH and OD spectra.

C. Energy Storage in Polyatomic Molecules

Several years ago we initiated under DOE sponsorship an investigation of the relaxation and reaction rates of vibrationally excited ozone, using $NO + O_3(001)$ as a prototype reaction.^{16,17} An interesting aspect of this research is the possibility of accelerating the rate of a reaction using a laser-excited inert gas sensitizer. In particular, we showed that vibrationally excited SF_6 can enhance the rate of $NO + O_3$.¹⁸

In the research described here we have examined the sensitization process in more detail. Specifically, the ν_3 mode of SF_6 was excited with a low power CO_2 laser (fluence $< 60 \text{ mJ/cm}^2$) in the presence of either NO or N_2O . Infra-red emission at $5 \mu\text{m}$ from the added species was monitored in real time using an InSb detector. A typical example for the time-resolved emission from $N_2O(00v)$ is shown in Fig 2. Measurements with a cold gas filter indicate that $> 75\%$ of the signal originates from $N_2O(001)$. The most striking aspect of the emission data is that the decay rate decreases with fluence, varying approximately as $(\text{fluence})^{-0.4}$. On the other hand

Figure 2. Typical IR fluorescence signal from a mixture consisting of 1.02 Torr N_2O and 0.031 Torr SF_6 . The fluence in the two traces was 57 mJ/cm^2 and 5.1 mJ/cm^2 . The average number of photons absorbed was, respectively, 5.4 and 0.46.

optical absorption measurements confirmed that the average amount of energy absorbed by SF_6 increases approximately linearly with fluence. The observed behavior, which was completely overlooked in previous fixed fluence experiments,¹⁹⁻²¹ can be understood in terms of energy storage within the SF_6 molecule.^{22,23} The N_2O emission is an indicator of the amount of energy in the ν_3 manifold of SF_6 . As the total amount of absorbed energy increases, the depletion time for SF_6 ($2\nu_3$) must correspondingly increase.

Another piece of information which can be obtained from this experiment is the rate of energy transfer from SF_6 to N_2O . From the risetime of the IR fluorescence we determined that the V-V rate constant decreases with fluence, and has a value of approximately $3 \times 10^4 \text{ sec}^{-1} \text{ Torr}^{-1}$ at 60 mJ/cm^2 .

D. Optoacoustic Detection of Infrared Multiphoton Excitation

Optoacoustic (OA) spectroscopy has been used for many years to measure single quantum relaxation rates in gases. In these experiments excitation is usually accomplished by a low intensity, chopped radiation source, while the relaxation rate is deduced from the phase shift in the resulting acoustic wave. Only recently has the OA technique been applied to multiphoton processes. In this case two unique difficulties arise. In order to relate the amplitude of the detected signal (S_{OA}) to the average number of photons absorbed ($\bar{n}$), an independent calibration is required. Also, the buffer gas which is required

to convert the excitation energy to a pressure pulse, can interfere with the photophysics of multiphoton absorption. Although the OA technique has been employed in a number of instances to measure $\bar{n}$, it has never to our knowledge been used to measure the relaxation rates of molecules subjected to multiphoton excitation.

During the past year²⁴ we have carried out a systematic study on the effects of laser fluence, substrate pressure, and buffer gas pressure on S_{OA} . The molecule cis-3,4-dichlorocyclobutene (DCCB) was chosen for this study for two reasons. First, it is large enough that buffer gas effects are unlikely to affect $\bar{n}$ significantly. Second it has an interesting chemical history. It was recently shown in this laboratory^{25,26} that at fluences above 3.5 J/cm^2 Woodward-Hoffmann forbidden isomerization products are formed. In order to model this multichannel effect, it is essential to determine the fluence and pressure dependence of $\bar{n}$.

The principle findings of this study are summarized as follows: (i) S_{OA} is proportional to the pressure of the absorber. (ii) S_{OA} increases monotonically with argon pressure up to approximately 20 Torr. At higher buffer gas pressures S_{OA} is constant. (iii) $\bar{n}$ is independent of pressure and increases approximately linearly with fluence (actually as $\phi^{0.815}$), reaching a value of 27 at $\phi = 8.2 \text{ J/cm}^2$. The variation of $\bar{n}$ with fluence is shown in Fig 3. The theoretical curve in this figure was calculated by John Barker, also with DOE support. The only empirical input to this calculation is

Figure 3. Average number of photons absorbed vs. laser fluence.

(a) Solid points are optoacoustic data taken with 32 mTorr of Ar. (b) The solid symbols are optoacoustic measurements taken with 101 Torr of argon. The circles are for 256 mTorr of DCCB using a 0.23 cm collimator, while the squares are for 225 mTorr of DCCB taken with a 0.47 cm collimator. The open circles are optical absorption measurements taken with 0.5 to 2.0 Torr of DCCB. The arrows in each panel indicate the fluences at which the optoacoustic measurements were calibrated. The solid lines are least squares log-log fits of the data. The dashed lines are stochastic solutions of the master equation, with error bars indicating the statistical uncertainty in the calculation.

the small signal cross section (measured by FTIR spectroscopy), which we assumed to be independent of internal excitation energy, E . The pressure independence of $\bar{n}$ and the energy independence of the cross section appear to be characteristic of large molecules having little or no vibrational bottlenecks.

An important unanticipated finding of this study is that the pressure dependence of the time resolved signal can be used to deduce the vibrational relaxation rate, K , of the excited gas. The underlying reasoning is as follows. When the relaxation rate is much slower than the pressure independent acoustic propagation rate, the acoustic signal grows as²⁷

$$S_{OA}(t) = S_0 (1 - e^{-Kt}).$$

Superimposed on this envelope are radial and axial acoustic undulations. As K is increased by raising the pressure, the undulations grow in size. When the relaxation and acoustic rates are matched, the envelope structure disappears, and strong positive and negative undulations dominate the signal. The amplitude of the first acoustic maximum varies with pressure as

$$S_{OA} = S_0 (1 - e^{-\lambda g}),$$

where λ is an instrumental constant and g is the ratio of the vibrational relaxation rate to the acoustic propagation rate. Thus if λ is known, the bimolecular relaxation rate constant, k , can be determined. This quantity depends on E (or $\bar{n}$), and hence is a partially averaged microcanonical rate constant. Experimentally we find for DCCB that $k(\bar{n})$ decreases with $\bar{n}$, for essentially the same reason given for SF_6 in the previous section. We can interpret the relaxation rate in terms of a weak

collision mechanism. That is, we assume that an average amount of energy, $\langle \Delta E \rangle$, is removed in each collision of vibrationally excited DCCB with an unexcited molecule. If $\langle \Delta E \rangle$ is much smaller than the total internal energy, E , of the molecule, we would expect the relaxation time to increase with E . Moreover, from these data it should be possible to deduce how $\langle \Delta E \rangle$ varies with E . Preliminary results indicate that $\langle \Delta E \rangle$ increases with the level of excitation of the molecule. This is an important finding because until recently²⁸⁻³⁰ there has been no experimental evidence for a variable step size in unimolecular relaxation of excited molecules.

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Publications of DOE Sponsored Research

A. Refereed Papers

1. "Abstraction vs. Exchange in the Reaction of D + HCl," (with J. C. Miller, J. Chem. Phys. 76, 5167 (1982)).
2. "Kinetics of the Cl-H₂ System. II. Abstraction vs. Exchange in D + HCl,"² (with J. C. Miller), accepted by J. Chem. Phys.
3. "Kinetics of the Cl-H₂ System. III. The Isotope Effect in Cl + D₂," (with J. C. Miller), to be submitted to J. Chem. Phys. in Sept., 1982.
4. "Opto-Acoustic Measurements of Infrared Multiphoton Excitation of cis-3,4-Dichlorocyclobutene (with N. Presser and J. R. Barker), submitted to J. Chem. Phys.

B. Other publications and presentations

1. "Kinetics of the Cl-H₂ System, J. C. Miller, Ph.D. Thesis, (University of Illinois at Chicago, Sept. 1982).
2. "Kinetics of the Cl-H₂ System" (with J. C. Miller), 182nd National Meeting of the American Chemical Society, New York, August 23-28, 1981.
3. "Abstraction vs. Exchange in the Reaction D + HCl," (with J. C. Miller), XV Informal Conference on Photochemistry, Stanford, June 27-July 1, 1982.
4. "The Vibrational Relaxation of SF₆ by NO and O₃" (with Y. Vlahoyannis and N. Presser), 7th International Symposium on Gas Kinetics, Gottingen, August 23-27, 1982.