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LETTERS

Picosecond Photofragmentation of Tri- and Tetraatomic Molecules: Measurement of "State-to-State" Reaction Rates

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In this Letter, we report our first results on the picosecond measurements of state-to-state rates of reactions, involving threeand four-atom molecules. These photofragment reactions are ICN \rightarrow I + CN and NCNO \rightarrow NO + CN. In these experiments, we use one picosecond pulse to initiate the photolysis and a second pulse to probe the produced fragments in their internal vibrational/rotational states. Results are presented for molecules in bulbs and beams, and comparisons with unimolecular theories are given.

Introduction

With tunable high-resolution lasers it is now possible to obtain details of internal energy distributions in the products of a chemical reaction.¹⁻³ In beams, the rates for these "half-collision" processes from an initial state i to a final state f (state-to-state rate; k_{if}) are obtained from knowledge of the reactive cross section $\sigma_{\rm fi}$ and the relative velocities.^{4,5} Vibrational and rotational energy resolution of the initial and final state of the photofragmentation allows one to examine the high-resolution state-to-state energy disposal in the fragments. Three- and four-atom molecules provide an opportunity for careful examination of these processes since the number of degrees of freedom is relatively small, and the atom or diatom produced in the reaction can be characterized spectroscopically, as shown recently in work on, e.g., H₂O, NO₂, HONO, NCNO, and CH₃I.6

Picosecond monitoring of chemical reactions in supersonic beams is an approach which we have taken recently for the detection of reaction products in *real time*, and for the measurement of state-to-state rates.^{7,8} Basically, one picosecond pulse prepares the reagent in a well-defined state, while the second pulse monitors the fragments in their different internal states. Using two-color picosecond pulses in a molecular beam with MPI/TOF, we have recently reported on the picosecond photofragmentation dynamics of CH₃I, CF₂I-CF₂I, and some van der Waals complexes.^{7,8} In the case of CH₃I, for example, the iodine atom was detected in either the spin-orbit 1/2 or 3/2 states as a function of the delay

time between the photolysis and probing pulses.

In this Letter, we report our first results on the direct measurement of state-to-state rates of the following reactions involving three- and four-atom molecules:

$$I-CN \rightarrow CN + I$$

$$NC-NO \rightarrow CN + NO$$

The probe pulse in this case monitors either fragments of the reaction (in their vibrational/rotational internal states) with a temporal resolution of $\sim 2-5$ ps and a rotational energy resolution that allows us to measure k(E,N), the rate of the reaction for a specified initial state (reagent) energy E to a final (product) rovibrational state N. This is achieved by monitoring laser-induced fluorescence or ionization of the produced fragments, while varying the delay time between the photolysis and probe picosecond pulses.

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Figure 1. Energy level scheme for the photodissociation of NCNO with product state detection. The two picosecond pulses depicted are for photolysis and probing.

The scheme for the experiments is depicted in Figure 1. Direct measurements of state-to-state dynamics allows for temporal resolution of reaction intermediates (and transition states), studies of the dependence of k(E,N) on vibrational and rotational energy contents, and real tests of unimolecular reaction theories.

Experimental Section

Picosecond Photolysis and Probe Experiments. The experimental arrangement for these picosecond pump-probe experiments is shown in Figure 2. The picosecond pulses are generated by an amplified synchronously pumped mode-locked dye laser. An actively mode-locked Ar⁺ ion laser synchronously pumps an R6G dye laser yielding tunable picosecond pulses at 82 MHz with pulse energies of ~ 1 nJ. These pulses are amplified in a three-stage dye amplifier pumped by the second harmonic of a Nd:YAG laser at 20 Hz (140 mJ/pulse). The resulting dye laser pulse energy is 0.5-0.7 mJ/pulse. The width is 2-5 ps.

In general, the probe pulse monitors the fragments by using either multiphoton (TOF) ionization or laser-induced fluorescence. For the CN radicals, laser-induced fluorescence of the $B \leftarrow X$ transition was used (band head of 0-0 transition at 3883.4 Å). This transition has often been used for monitoring CN because of the high sensitivity afforded as well as the uncongested rotational envelope which allows monitoring of individual CN rotational states.⁹ As illustrated in Figure 2, the 3883.4-Å wavelength is generated by mixing, in a KDP crystal, the dye laser pulses, \sim 6116 Å, with the 1.06- μ m fundamental of the amplifying YAG laser. The dye laser could be tuned so that any of the rotational transitions in the $B(v'=0) \leftarrow X(v''=0)$ band could be probed.

The pump for ICN was the frequency doubled dye laser, and for NCNO either the dye laser fundamental or the doubled dye laser was used. In either case they are not independently tunable but are determined by the probe frequency. Finally, one other arrangement was used for the NCNO experiments in order to shift the pump pulse frequency significantly. The dye laser was tuned to \sim 5938 Å and focussed into a 1-m high-pressure (130 psi) cell containing methane for the purpose of Raman shifting. The Stokes shifted radiation (-2914 cm⁻¹) was then frequency doubled ($\lambda =$

3590 Å) and used to probe the CN $B(v'=1) \leftarrow X(v''=0)$ transition. In all cases the general optical arrangement was the same as shown in Figure 2. The nonlinear processes were used to generate the probe, and the pump and probe were separated by a dichroic mirror. The pump travels a fixed delay while the probe is directed to a variable delay arm before they are recombined with a second dichroic mirror. The collinear beams are overlapped in the sample, bulb or beam, and optimized by maximizing the laser-induced fluorescence at positive delay times. The enhancement of signal from both beams together was approximately a factor of 10 over the signal from the pump and probe separately. This was limited by scattered light from the probe which could not be biased against because strong $\Delta \nu = 0$ Franck-Condon factors in the CN transition dictated that resonance fluorescence be collected. A Corning 7-54 filter was used to block any scatter from the visible pump pulse and a WG360 filter blocked UV pump pulses. For NO and I detection¹⁰ we used the time-of-flight MPI detection described in ref 7 and 8.

Sample Handling in Bulb and Beam Experiments. For bulb experiments, a glass cell with quartz entrance, exit, and fluorescence viewing port windows was used. ICN (Kodak) was purified by vacuum sublimation and used in the fluorescence cell at room temperature (vapor pressure $\simeq 1$ torr). NCNO is not commercially available and so was synthesized by using a published procedure.¹¹ It is formed in a one-step reaction of nitrosyl chloride (NOCl) with dry AgCN at -40 to -30 °C on a vacuum line. The NCNO product is then trapped at liquid N_2 temperature but is contaminated by a large amount of the NOCl reactant. The NCNO is then purified by repeated distillation from pentane/ liquid N_2 (142 K) or hexane/liquid N_2 (179 K) slush baths. An absorption spectrum (Cary-14) of the NCNO product was found to be identical with the published spectrum.¹² However, it is known that NO_x impurities are always present. Although no explosions occurred, due caution was taken in handling the NCNO as several reports of spontaneous detonation have been made.¹²

NCNO is a gas at room temperature and highly reactive in the presence of metals, so all sample handling had to be with teflon or glass. In the room temperature cell a small amount of NCNO was trapped into a bulb at liquid N2 temperature and then allowed to expand into the evacuated cell to a final pressure of ~ 2 torr.

Several experiments were performed in a beam apparatus employing a pulsed nozzle. This nozzle was made from Kel-F, a perfluorinated plastic, to prevent reactivity with the NCNO samples. An appropriate amount of NCNO was transferred to a 5-L bulb and again allowed to expand to a final pressure of 5-10 torr. This bulb was connected to the pulsed valve by teflon tubing and provided a large enough reservoir for the duration of an experiment. Supersonic expansion experiments were not possible for ICN or NCNO because in both cases the pump wavelengths available were not energetic enough to directly reach the dissociative states but required the thermal energy available at room temperature to excite above the dissociation threshold.

The Systems Studied

ICN: "Direct" Fragmentation. As with methyl iodide, it is now established that ICN when excited to the A continuum produces¹³ the I atom in both the ground I $(^{3}/_{2}$ state) and excited I* $(^{1}/_{2}$

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PICOSECOND APPARATUS



Figure 2. Schematic diagram showing the general experimental arrangement for picosecond photolysis-probe experiments: DC, dye cell; SF, spatial filter; CL, cylindrical lens; BD, beam dump.

state) states. The CN is produced in the $X^2\Sigma^+$ state. The branching ratio of I are I* are known, and there is very little vibrational excitation in the CN. The rotational excitation in the CN is quite interesting. For example, for 266-nm photolysis, mostly low N" states are populated but there is some broad distribution of high N". Whether this is due to complicated reaction pathway or due to different surfaces (of bent and linear ICN) is in question. Recent studies by Wittig's group¹³ indicate that the low and high N" derive from linear and bent exit channel geometries, respectively; high N" are selectively produced in the I production channel, whereas low N" distribution is associated with I* production. They also found that the spatial anisotropy β is high (1.3-1.6) for both I and I* formation (for the initial excitation of a parallel transition(s)), consistent with the early work of Wilson's group.¹³

NCNO Fragmentation: Predissociation. The reaction of NCNO to give NO(X) and CN(X) has been studied by Wittig's group¹⁴ and by Pfab et al.¹⁵ The spectroscopy of the nascent CN and NO fragments has been thoroughly documented for the molecules in bulbs and in supersonic jet expansions.¹⁴ The vibrational, rotational, and translational energy distributions are known. Very little vibrational excitation is produced, and the CN fragment is in its electronic ground state.

From our point of view, this reaction is an ideal system to study for a number of reasons. First, the reagent excitation is to a "localized" state on the NO part of the molecule, and to break the bond, energy redistribution is required. Because the spectrum of this molecule in the red region is structured predissociation is expected, and we anticipated seeing the dynamics of this bond breakage on our picosecond time scale. Second, the CN and NO fragments are rotors of similar masses, and the vibrational-rotational energy distribution in the $CN(X^2\Sigma^+)$ is believed to be statistical. If vibrational predissociation is from a loosely bound transition state involving S_1 or S_0 surfaces the picosecond dynamics of this reaction should eludicate the nature of the transition state. Third, because the spectroscopy of the CN fragment is known and the spacings of the rotational levels are well-resolved, our experiments should provide details of k(E,N'') as we tune the probe across the different N'' states of the products. Hence, details of the angular momentum selection rules can be obtained, and tests of reaction rate theory can be made.

Results and Discussions

Figure 3 displays the picosecond transients obtained for ICN in an effusive beam and in a bulb. Detecting the CN at low N''(~0), $\lambda_{\text{probe}} = 3875$ Å, or at high N''(~35), $\lambda_{\text{probe}} = 3843.5$ Å, yields essentially the same transient. In the beam (see Figure 3) detection of CN at the band head ($N'' \sim 25$), $\lambda_{\text{probe}} = 3883.4$ Å, gives a prompt buildup of CN fluorescence. All three transients indicate that the CN fragment is formed (low and high N'') on a very short time scale. The iodine signal, detected by 2+1 MPI/TOF, also rises very rapidly, within the temporal resolution of our apparatus. It is interesting to compare these findings with those obtained using "CW" photofragment techniques.

The fragmentation of the triatomic ICN can be viewed on a repulsive surface with the I atom and CN radical recoiling along the molecular axis. For parallel transitions, the spatial anisotropy, β , is classically expressed as

$$\beta = 2 \frac{1 + (\omega \tau)^2}{1 + 4(\omega \tau)^2}$$

where τ is the dissociation lifetime and ω is the angular rotational frequency. β has been obtained by Nadler et al.¹³ to be 1.3 for I and 1.6 for I* which are high; slightly below the maximum value of 2 expected in this case. This infers that a τ of 200 and 100 fs is expected for the ICN excited states that lead to I and I*. For the I + CN route, high N" are selectively produced, whereas for the I* + CN channel the N" distribution of the CN peaks sharply at low N". The fact that we see both the high and low N" states build up in less than 5 ps is consistent with the spatial anisotropy measurement and with the distribution of the CN.

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Figure 3. Laser-induced fluorescence signals of CN produced by the one-photon UV photolysis of ICN. The horizontal scale is the delay time between the photolysis pulse, ~ 3058 Å, and the probe pulse, ~ 3883 Å, which is tuned over a small range to sample different CN product rotational states. The top trace is an effusive beam transient (as a comparison with bulb conditions (1 torr of ICN)).

Further experiments are in progress to resolve differences in the rates for I and I* production (see Note Added in Proof).

In contrast to ICN, the fragmentation of NCNO shows a very slow (on the picosecond time scale) rise. Furthermore, the rates for CN production depends on the N'' levels detected. In Figure 4 and 5, we display results obtained for NCNO in beams and bulbs. Detection of the CN in low N''(2) gives a rate of (90 ps)⁻¹, whereas high N''(27) detection gives $(10 \text{ ps})^{-1}$. This change in rates as we tuned across the N'' spectrum is very pronounced as the data in Figure 5 shows. In the above experiments on NCNO the photolysis pulse was tuned to the red part of the spectrum (6040-6117 Å). In this case, the LIF intensity of the CN was found to be linearly dependent on the intensity of the red photolysis pulse, consistent with the result of ref 12b which indicates that at this wavelength there is no significant CN produced by twophoton red excitation. When the photolysis pulse was tuned to the UV (direct absorption to a higher excited state), the buildup of the CN fragment became instantaneous, as shown in Figure 4. The single- and two-photon dissociation of NCNO is discussed in the paper by Nadler et al.^{12b} Our one-photon UV photolysis experiment corresponds to the wavelength of two-photon excitation, and the rapid buildup of the CN fragment indicates that this state is directly dissociating, similar to ICN. The predissociation observed from the red photolysis pulse is state dependent and must relate to the photodissociation vibrational/rotational dynamics on the surface producing CN and NO.

The dissociation energy of NCNO to CN and NO is 48.8 kcal/mol (17085 cm⁻¹). The recoil of the two coupled rotors, NO and CN, will produce small rotational excitation if the fragmentation is collinear. From the studies made by Wittig's group it is now clear that excitation of the parent near dissociation results in CN almost completely cold (90% of the molecules are in the N'' = 0 state). However, as the total energy increases high N''



Figure 4. Comparison of picosecond transients for visible and UV photolysis of NCNO. Except for photolysis wavelength the experimental conditions are identical. The rise of CN in N'' = 10 state with visible photolysis is 45 ps but with UV photolysis it becomes faster than our system response.

states are fully populated. (The vibrational excitation in both cases is close to zero.)

There are two interesting and basic questions pertinent to the picosecond dynamics of NCNO predissociation: (1) Why are the rates N'' dependent? (2) Given the total energy for dissociation, why are the rates relatively slow? In the center of mass of the parent, there are nine degrees of freedom; six vibrational and three rotational. These become two vibrational, four rotational, and three translational product degrees of freedom. Knowing the vibrational modes in the parent, we have calculated¹⁶ the total density of states (assuming harmonic approximation) to be the following: $\rho = 288$ per cm⁻¹ at a total energy of 17135 cm⁻¹ (50 cm⁻¹ excess energy above dissociation); 368 per cm⁻¹ at 18135 cm^{-1} (1050 cm^{-1} excess energy); and 465 per cm^{-1} at 19135 cm^{-1} $(2050 \text{ cm}^{-1} \text{ excess energy})$. To address the second question we performed standard RRKM calculation to obtain some ideas about the magnitudes of the rates, even though we are aware of two problems in applying the RRKM to this class of reactions. First, **RRKM** does not give the dependence of rates on product N''. Second, the transition state for this reaction does not warrant the use of standard RRKM, and one should use phase space theory,¹⁷ ACM,¹⁸ or modified RRKM¹⁹ or phase space theory.²⁰ Nev-

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Figure 5. Laser-induced fluorescence signals of CN produced by the one-photon visible photolysis of NCNO. In the top trace the N'' = 2 rotational state of the CN products is probed and shows a rise time of 95 ps. by probing N'' = 20, lower trace, the rise time decreases dramatically to 20 ps. These transients were obtained in an effusive beam, but identical results were obtained in a bulb at 2 torr.

ertheless, using standard RRKM,¹⁶ one obtains the following k(E) rates:²¹ (10 ns)⁻¹ at 50 cm⁻¹ above dissociation; (685 ps)⁻¹ at 1050 cm⁻¹; and (177 ps)⁻¹ at 2050 cm⁻¹. If, however, we reduce three of the frequencies in the transition state²² by a factor of 2, then these rates become (10 ns)⁻¹, (130 ps)⁻¹, and (29 ps)⁻¹ for the excess energies given above, respectively. Clearly, k(E) depends markedly on the excess energy in the reagent, a point that we will discuss shortly.

The observed dependence of the rates on N'' (see Figure 6) could be explained in one of two ways. Conservation of angular momentum during predissociation may result in varying rates for different product quantum states being populated. Alternatively, the dominant contribution to the population in different product N'' states may be derived from different energy ranges in the thermal distribution of the reactant. The observed rates would then be demonstrating an energy dependence only. Since our experiments were performed on a room temperature sample (bulb or effusive beam), any state-specific effects will be masked by unavoidable ensemble averaging. The average vibrational energy of NCNO at 298 K is 275 cm⁻¹ and the distribution function is monotonically decreasing with energy. The rotational distribution is broadly peaked about J = 25. We have performed phase space theory calculations to predict CN(N') distributions for a range of excess energies $(0-2000 \text{ cm}^{-1})$ and angular momenta (J =



Figure 6. Dependence of the measured rates on N'' for two different excitation arrangements, as discussed in the text. For the last point (N'' = 27), the rate given is a lower limit.

15-30). A Boltzmann weighted average of the contribution to specific CN(N') channels as a function of reactant energy and J showed that the major contribution to a given channel is from energies close to the threshold for that particular channel. If thermal energy effects were to explain the apparent N'' dependence completely, k(E) would have to change by an order of magnitude over ~1000 cm⁻¹ (the threshold for CN(N''=20)). The rates calculated (RRKM) indicate this is possible provided we modify the transition-state frequencies drastically, as mentioned above.

Experiments probing different N'' while holding the energy in the reactant fixed are in progress. This series of experiments will allow us to distinguish between the two cases conclusively and, more importantly, correlate the rates with details of the transition state and angular momentum constraints. We also plan to examine the effect of $S_1 \rightarrow S_0$ energy redistribution on the observed rates, and the sensitivity of these rates to the initial J state excited.

In conclusion, these first picosecond photolysis and probe experiments in beams offer new opportunities for examining state-to-state (real time) dynamics of chemical reactions, and for learning about the transition state on these ultrashort time scales. Product state detection of atoms and diatoms by MPI or LIF allows for picosecond resolution of rates to specific and well-defined states. We hope to report shortly on similar experiments on the femtosecond time scale as well as experiments on other systems, especially those studied by Zare and Dixon,²³ for which thorough studies of internal energy distribution exist.

Note Added in Proof: Very recently we have compressed the pulses of our dye laser (Figure 2) for femtosecond time resolution of the ICN transients. Preliminary results were obtained for 306-nm photolysis and 388-nm probing; the rise time for CN formation is ~ 500 fs. This gives rise to a β of ~ 1.3 . Further details of this work will be published soon.²⁴

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⁽²¹⁾ Note that we have dropped the N" index because, as stated in the text, RRKM does not explicitly provide k(E,N').

⁽²²⁾ As a first approximation of the loose transition state we have reduced the vibrational frequencies by a factor of two for motions containing the dissociation coordinate, i.e., C-N=O and N=C-N bends and the out-of-plane wag.

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