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Time-resolved infrared absorption studies applied to the study of radical plus molecule reactions*

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ABSTRACT

The reaction of the cyano radical (CN) with ethane (C₂H₆) was studied using time resolved infrared absorption to monitor the product hydrogen cyanide (HCN) in individual ro-vibrational states. Pulse laser photolysis was used to provide an initial excess of the CN radical and the time dependence of individual ro-vibrational states of the high frequency anti-symmetric stretching mode of HCN (0,0,v₃) was followed. These experiments reveal that the initial product state distribution of HCN is not highly excited in the HCN(0,0,v₃) vibrational manifold.

1. INTRODUCTION

There is a wealth of information available about product state distributions from atom + molecule reactions¹ and these results in conjunction with theoretical models have been used to greatly increase our understanding of the dynamics of chemical reactions. This is especially true for F atom reactions probed by the infrared chemiluminescence technique.² Indeed, infrared chemiluminescence has been and, continues³ to be a powerful probe for the elucidation of the dynamics of chemical reactions. The abstraction of an H atom by F from a wide variety of donor molecules to give vibrationally excited HF(v,J) has proved to be a particularly valuable tool in illuminating many aspects of chemical dynamics. However, despite the progress that has been made over the last few decades there is still a considerable lack of detailed state-specific information on reactions that produce a polyatomic product.⁴ The reaction CN + O₂ → NCO + O is only one of a few reactions in which the internal state distribution of a polyatomic reaction product has been almost fully determined.⁵ Unlike NCO, many simple polyatomic molecules do not have excited electronic states that are in a convenient wavelength region or appropriate for the application of the powerful laser-induced fluorescence (LIF) method; on the other hand, all molecules have active infrared absorptions so that infrared techniques have become increasingly popular⁶ in probing the product state distributions of polyatomic fragments.⁷

In the present work the reaction

was studied using time resolved infrared absorption to probe the state distribution of the linear polyatomic fragment, HCN. The CN radical behaves chemically much like a F atom and it is hoped that a comparison between the dynamics of the analogous F atom hydrogen abstraction reaction⁸ will provide an interesting comparison to the dynamics of Reaction (1).

Reaction (1) and related reactions have been studied in several different laboratories^{9,10} usually by using a pulse-probe method that follows the decay of the CN radical detected by LIF. Jackson and coworkers¹¹ have also studied the infrared chemiluminescence from the HCN product. The rate constant measurements of all groups are in excellent agreement and temperature dependence of the rate constant showed substantial non-Arrhenius behavior. The exact

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explanation of this non-Arrhenius behavior is uncertain at this time. At 294 K Hess et al⁹ found that k_1 was $2.81 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This is almost $1/10$ a hard sphere collision rate constant so that reaction into a specific internal vibrational state of HCN could effectively compete with vibrational relaxation if the number of internal states of HCN initially populated in Reaction (1) were small. Smith and Warr¹¹ have measured the vibrational relaxation rate constants for HCN(011), HCN(101) and HCN(001) by C_2H_6 and found that the collisional probability varied from $1.95 \cdot 10^{-2}$ to $3.3 \cdot 10^{-3}$, respectively.

Some important concepts in chemical dynamics are vibrational adiabacity¹² and the effectiveness of vibrational energy in accelerating chemical reactions¹³. By using different precursors as the source of the photolytic CN radicals the initial vibrational energy content of CN can be varied and the change in the HCN internal state distribution followed. Preliminary evidence for the adiabatic nature of the CN vibrational mode in Reaction (1) will also be presented.

2. EXPERIMENTAL

The experiments were carried out in a transverse flow reactor (TFR), which consisted of a teflon box 100 cm long, 100 cm wide and 5 cm in height. This teflon box was housed in a vacuum tight stainless steel vessel. In the present experiments the TFR was evacuated by a liquid nitrogen trapped 20 cfm mechanical pump. The probe and photolysis lasers crossed the reaction gas mixture perpendicular to the gas flow direction. This arrangement allows for rapid removal of photolysis products between photolysis laser pulses. The tunable infrared probe laser was a Burleigh Model 20 single mode color center laser. The color center laser was pumped by a LaserIonics a continuous 4 watt Kr^+ ion laser. The pulse of CN radicals that initiated Reaction (1) was produced by 193 nm excimer laser photolysis of either BrCN or ClCN . Gases were continuously flowed through the TFR and partial pressures were determined from their molar flow rates, as determined by calibrated Gilmont Rotameters, and total pressure. The pressure in the TFR was measured by appropriate pressure transducers, Datametrics Model 600 (1 to 10 torr) and or MKS type 227 (0 to 2 torr). The absorbances measured in this experiment are small, less than a few percent, and the largest source of noise was amplitude fluctuations of the probe infrared laser. In order to reduce this source of noise differential detection of the time dependent absorption signal was used. The infrared beam was split into two, one channel determined the initial light intensity, I_0 and the other the transmitted intensity, I . Both channels were detected by matched liquid nitrogen cooled InSb infrared detectors. The signals were then combined and amplified by a fast response differential amplifier. The frequency response of the combined infrared detector, differential amplifier combination was greater than 5 MHz. The amplified absorption signal was then signal averaged on a LeCroy Model 9410 Digital Oscilloscope.

The infrared laser linewidth is much narrower than the Doppler width of HCN at 294 K (FWHM 300 MHz); however, the laser can mode hop (spacing 300 MHz) with a resulting loss in signal. To ensure that the laser was tuned to line center over the course of recording a signal averaged trace, the following approach was taken. A box car averager was used to monitor the maximum absorption signal in the time profile of the absorption trace and as data collection proceeded the color center wavelength was manually tuned to maximize the box car signal.

The infrared and excimer lasers were spatially overlapped using a dichroic mirror. The spatially overlapped laser beams were admitted into the TFR through Brewster angle windows. Although part of the inert gas flow, usually Ar, flowed was diverted and flushed the region of the Brewster angle windows, at low pressures, less than one torr, photolysis products were deposited on the windows. In order to account for the possible loss in excimer laser intensity, the incident and transmitted ArF laser intensity was detected by Si PIN photodiodes and ratioed using a box car averager. For most of the experiments the loss in ArF power was less than 5% over the course of the experimental run and no correction was applied to the data. The excimer laser power was varied between 10 and 50 millijoule/pulse in a beam of approximate size $3 \times 1 \text{ cm}$, and the excimer laser beam was directed away from I channel detector and the beam. The excimer laser beam profile was rotated through 90° so that it traversed the TFR with the long beam axis vertical.

3. RESULTS

In any absorption experiment the quantity actually measured is the population difference between the lower and upper quantum states connected by the radiative transition and not the lower state population directly. In the present experiments the inert gas pressure was sufficiently high that translational equilibrium was always maintained and the pressures low enough (less than 5 torr) that the line shape of HCN was well described by a Doppler profile. As mentioned in Section 2 care was taken to ensure that the probe laser was tuned to line center so that the observed absorbance $\ln(I_0/I)$ was directly related to the population difference. The HCN transitions probed in this work did not involve the bending vibration so that they are all $\Sigma - \Sigma$ type bands having P and R branches only. The majority of the transitions probed were all R branch transitions because of their slightly larger line strengths; hence the absorbance, at any time t , is given simply by

$$\ln(I_0/I) = \epsilon l \{ N_v(j'') - N_{v+1}(j''+1) \} \quad (2)$$

where ϵ is the peak absorption cross section,¹⁴ l the path length and $N_v(j'')$ is the population in the lower vibrational level in rotational state j'' and $N_{v+1}(j''+1)$ is the population in the upper vibrational level at time t . Successive measurements of $R(j''+1)$ branch transitions with increasing vibrational and rotational quantum numbers were made to a final vibrational level, v_f , in which there is no population in the $N_{v_f+1}(j''+1)$ state. This last measurement determines the population in level v_f directly. Successively adding N to N_v gives the population in each individual ro-vibrational level for the series N_0 to N_{v_f} .

As mentioned in the Introduction, one of the aims of this work was to explore the influence of the CN vibrational motion on Reaction (1). To this end two different sources of the CN radical were used, either BrCN or ClCN. The 193 nm photolysis of BrCN produces CN radicals almost exclusively in the $v=0$ state, while photolysis of ClCN produces at least 50% of the CN radicals in vibrationally excited levels.¹⁵ Unfortunately, both sources produce CN highly rotationally excited. In order to at least have some understanding of the influence of the various factors on Reaction (1) and to greatly simplify the determination of vibrational state populations, the experiments were carried out at relatively high pressures so that rotational relaxation of both reagent CN radicals and product HCN molecules would be complete on a time scale faster than either reaction or vibrational relaxation. Under these circumstances it is only necessary to probe a single series of transitions, such as illustrated by Equation (2), in order to extract the vibrational state distribution because the rotational degree of freedom is assumed to be a Boltzmann distribution characterized by the ambient temperature of 294K.

One of the chief difficulties in studying the state distribution of polyatomic reaction products is the large number of possible product states. If the reaction dynamics and/or kinematics are favorable then perhaps only a few specific modes may be excited and the population in these modes would be sufficient to detect. On the other hand, a large number of final quantum states may be populated making their detection difficult because of the small initial population in each individual level. For Reaction(1) the high frequency anti-symmetric stretching mode, v_3 , which primarily corresponds to vibration of the H atom against the C atom, might, at first glance, be closely associated to motion along the "reaction coordinate" and be significantly populated in the reaction. Thus, as a first test, the HCN(0, 0, v_3) vibrational manifold was probed. For rotationally relaxed CN($v=0$), the exothermicity of Reaction (1) limits HCN(0, 0, 2) to be the highest accessible level of this manifold. Assuming rotational relaxation of both CN and HCN the time dependence of the vibrational state distribution HCN(0, 0, v_3) manifold was determined under a variety of conditions. An advantage of an absorption technique over an emission one is that the population in the ground state may be measured. This allows for a direct comparison of the population in level (0, 0, v_3) to that in (0, 0, 0) at each instant in time. As mentioned previously the thermal rate constant, k_1 , for Reaction (1) is well established and the value reported by Hess et al.⁹ was used in this work. After a sufficiently long time after the initial photolysis pulse but before diffusion has removed HCN from the probe beam the total HCN concentration, $[HCN_T(t=\infty)]$ was determined from the maximum in the HCN(0, 0, 0) absorption profile. Using the known k_1 value the time dependence of the total HCN concentration is given by

$$[HCN_T(t)] = [HCN_T(t=\infty)] \{ 1 - \exp(-k_1[C_2H_6] t) \} \quad (3)$$

This expression for the total HCN produced in Reaction (1) was used to express the population in HCN(0,0,1) and HCN(0,0,2) as a fraction of the total HCN population at time t , i.e., $[HCN(0,0,v_3)] / [HCN_T(t)]$. A typical determination of this initial fraction is shown in Fig. 1.. If the cross section for producing any state of the (0,0, v_3) manifold from Reaction(1) were large, then this fraction might be expected to be constant for some period of time before relaxation degraded the initial population.. Under these circumstances, an extrapolation to $t=0$ should yield the initial vibrational state distribution of HCN (0, 0, v_3). The uncertainty is large for reaction times close to the initial photolysis pulse especially for the determination of HCN(0, 0, 0) because this state requires the sequential addition of the population in HCN(0, 0, 2) and HCN(0, 0, 1). The conditions in Fig. 1 high inert gas pressure and low C_2H_6 pressure should provide the best estimate of the initial state distribution for the HCN(0,0, v_3) manifold. It was found that the initial vibrational state populations were HCN(0,0,2) = 2%, HCN(0,0,1) = 1% and HCN(0,0,0) is not populated at all directly from Reaction (1). Other experiments, under different experimental conditions indicate similar results. It is clear from Fig. 1 that as time proceeds relaxation of the HCN(v_1 , v_2 , v_3) levels that are initially populated by Reaction (1) produces population in the HCN(0, 0, v_3) manifold. One of goals of this type of study is to try and unravel these relaxation pathways, as will be discussed shortly.

Figure 1. The determination of the initial vibrational state distribution for the $\text{HCN}(0,0,v_3)$ manifold from Reaction (1). The conditions of this experiment were $P_{\text{Ar}} = 5.267$, $P_{\text{C}_2\text{H}_6} = 0.0676$ and $P_{\text{BrCN}} = 0.0710$ torr. On the left hand Y-axis is plotted the fraction of $[\text{HCN}(0,0,v_3)]$ of the total $[\text{HCN}_T(t)]$ that was produced up to that instant in time. For reference, on the right hand Y-axis, shown by the heavy line, is plotted the extent of reaction, Equation (3). State populations were determined from absorbance measurements as outlined in the text.

The vibrational energy content of the CN radical was varied by photolyzing either BrCN, producing $\text{CN}(v=0)$, or ClCN, producing 50% $\text{CN}(v=0)$ and 50% $\text{CN}(v>0)$.¹⁵ A direct comparison of the influence of CN vibrational excitation is shown in Fig 2 and 3. The exothermicity and initial energy content of the reactants is sufficient to populate the $\text{HCN}(2, 0, 1)$ level in Reaction (1). For $\text{CN}(v=0)$ reactant, there is not enough energy to populate the upper state in the radiative transition, $\text{HCN}(2, 0, 2)$, used to monitor the time dependence of $\text{HCN}(2, 0, 1)$ and the absorbance is a direct measure of the population in a single ro-vibrational state of $\text{HCN}(2, 0, 1)$. Although the absorption coefficients of both BrCN and ClCN at 193 nm are small there is a significant perturbation of the absorption temporal profile especially for small absorbances that it was necessary to record a background trace with the infrared laser tuned off of the absorption line. This background trace was subsequently subtracted from the absorption trace with the probe laser tuned to line center. The traces shown in Fig. 2 and 3 were treated in this fashion. The experimental conditions were identical for each Fig. except that the partial pressure of ClCN was slightly higher, Fig. 3. To account for this and the difference in the absorption coefficient at 193 nm between BrCN and ClCN, the traces have been normalized to the final $[\text{HCN}_T(t=\infty)]$ so that a direct comparison for the production of $\text{HCN}(2, 0, 1)$ can be made. It is clear that there is a significant enhancement in the production of this vibrational mode when CN is vibrationally excited. For $\text{CN}(v=2)$ reactant it is possible to produce $\text{HCN}(2, 0, 2)$ and the absorption profiles such as shown in Fig. 4 may be perturbed because of this. Further efforts are needed to clarify the exact dynamical cause of this enhancement in production of $\text{HCN}(2, 0, 1)$ with vibrational excitation of CN.

The kinetics of any individual HCN vibrational level is complicated because of the large number of possible relaxation pathways. Except for the most energetic vibrational level, any $\text{HCN}(v_1, v_2, v_3)$ may be populated either directly from Reaction (1) or by vibrational relaxation induced primarily in collisions with C_2H_6 . Nothing is known about any preferential relaxation pathways or the magnitude of processes involving multiple vibrational quantum number changes. It is one of the goals of this work to try and identify those relaxation processes that are more efficient than others. For example consider only a few possible pathways for relaxation of the $\text{HCN}(2,0,1)$ level.

Production

(4)

Removal

Equations (4) to (7) are only a small subset of all the possible relaxation processes for the removal of HCN(2, 0, 1). If the rate equations for the time dependence of HCN(2,0,1) are solved then the HCN(2,0,1) as a function of time should be described by two exponential terms with time constants describing Reaction (1) rate and the total removal rate, i.e. the sum of all possible relaxation rate processes such as Equations (5) to (7) and preexponential factors of opposite sign. However, the description is not quite as simple as that and there are several other vibrational states that could populate HCN(2,0,1) by relaxation, such as HCN(1,3^{1,3}, 1) as well as rotational levels of slightly less energetic vibrational levels such as HCN(0,1,2). For reaction of vibrationally excited CN(v>0) many more levels could be populated and HCN(2,0,1) produced by relaxation of more energetic states. As a result the time dependence of HCN(2,0,1), which is proportional to the time dependence of the absorbance, (Equation (2)), was fit to a series of three exponential terms of the following form

$$[\text{HCN}(2,0,1)(t)] = A_s \exp(-k_s t) + A_f \exp(-k_f t) - A_r \exp(-k_r t) \quad (8)$$

The positive preexponential factors are determined primarily by the time dependence after the maximum in the temporal profile, while the negative term is determined by the time dependence before the maximum. An example of the C₂H₆ pressure, P C₂H₆, dependence of these various rate processes is shown in Fig. 4. This data was measured under very similar conditions except for the variation in the pressure of P

Figure 2. Time-resolved absorbance of HCN(2,0,1) produced in Reaction (1) following the photolysis of BrCN. The pressures of the various gases were P Ar=2.278, PC₂H₆ = 0.155 and P BrCN = 0.142 torr.

Figure 3. Time-resolved absorbance of HCN(2,0,1) produced in Reaction (1) following the photolysis of ClCN under conditions similar to those of Fig. 2.

Figure 4. Measured exponential rates for HCN(2,0,1) from reaction of CN(v) following the photolysis of ClCN. The rates were determined by a non-linear least squares fit to absorbance curves similar to Fig. 3 using the model function given by Equation (8).

The slopes of such plots should yield a bimolecular rate constant for C₂H₆ for the process, if any, that can be associated with that rate. The values of these slopes, interpreted as bimolecular rate constants, are $k_s = 7.4 \times 10^{-12}$, $k_f = 2.4 \times 10^{-11}$ and $k_r = 1.7 \times 10^{-11}$ cm³molecule⁻¹s⁻¹. The larger rate constant, k_f , is 15% smaller than the accepted value^{9,10} for the reaction rate for Reaction (1). At first glance it might be anticipated that the reaction rate should describe the appearance of HCN(2,0,1) and be associated with the initial portion of the temporal profile; however, the relative magnitudes of terms contributing to the preexponential factors are important and it is not *a priori* possible to predict which decay constant is to be associated with which rate process. This situation arises of course because the HCN(2,01) vibrational state is being populated by relaxation from more energetic levels formed in Reaction (1) as well as directly in Reaction (1). The term with the negative preexponential factor, should be a measure of the relaxation of more energetic levels contributing to HCN(2,01) formation. A term describing the total removal of HCN(2,0,1) should also be present. The slow rate process, k_s , may in fact describe this process, or it may reflect the time dependence of some relatively long-lived state or secondary reactions producing HCN. These questions are currently being investigated.

If k_f is the term related to the total rate of Reaction (1) and this seems likely, then it should be noted that the rate of CN($v > 0$) is very similar to that of CN($v = 0$) because the data presented in Fig. 4 was obtained from ClCN photolysis, which produces 50% of the CN radicals vibrationally excited.

4. DISCUSSION

Preliminary data on the state specific, time-resolved, infrared absorption measurements have been applied to the study of the reaction dynamics of Reaction(1). It is clear from the experimental results, Fig. 1 that the HCN(0,0, v_3) vibrational manifold is *not* substantially populated directly in this reaction. An advantage of an absorption technique is that

the time dependence of the ground vibrational state may be observed. This allows the observed populations to be expressed as a fraction of the total population of HCN produced in the reaction. Thus, it is clear that the cross sections for producing HCN with anti-symmetric stretching motion from Reaction (1) are quite small. Other vibrational modes must be excited because the ground state is not. Preliminary data on probing HCN vibrational states involving the symmetric vibration manifolds, $\text{HCN}(v_1, 0, v_3)$ indicates that the cross sections for producing these vibrational states are also small. By the process of elimination, it appears likely that a substantial amount of HCN bending motion is produced in Reaction (1). Work is in progress to verify this conjecture.

The CN radical behaves in many cases as a halogen atom and a comparison of the $\text{HF}(v)$ vibrational state distribution from the analogous $\text{F} + \text{C}_2\text{H}_6$ reaction is instructive for comparing the state distributions of diatomic molecule to that for polyatomic molecule. Bogan and Setser⁸ found substantial vibrational excitation in HF with the distribution $v=0, 1, 2, 3$ and 4 to be 0.01, 0.12, 0.51 and 0.36. The $\text{HF}(v=0)$ population was deduced from a surprisal analysis of their data. It is clear that there is substantial vibrational excitation in the HF product. In contrast to this the cross section for formation of $\text{HCN}(0,0,v_3)$ is very small; furthermore, the cross section for producing $\text{HCN}(0,0,0)$ appears to be zero, similar to the vibrational state distribution for the HF product. Thus both F and CN reactions with C_2H_6 produce almost exclusively vibrationally excited products.

The vibrational motion of CN might be expected to be a spectator throughout the course of Reaction (1) because the "reaction coordinate" would be expected to follow the motions between the transferring H atom and the C atom of the CN radical. Although the data presented in Fig. 2 and 3 can be interpreted to support the conservation of the CN vibration into vibrational motion of HCN primarily describing CN vibration, the enhancement in the $\text{HCN}(2,0,1)$ state with $\text{CN}(v>0)$ reagent could also be due to a conservation of vibrational energy and this state has an increased population due to relaxation from more energetic vibrational levels. Further work to resolve this issue is needed. The identification of k_f with the total reaction rate constant k_1 does indicate that vibrationally excited CN does not greatly enhance the thermal reaction rate.

It is instructive to compare Reaction (1) to a related reaction, $\text{CN} + \text{O}_2 \rightarrow \text{NCO} + \text{O}$. Dramatically different NCO product state distributions were found when this reaction was studied under molecular beam conditions, in which the reactants are prepared in their lowest rotational states, compared to thermal conditions, in which there is a broad distribution of possible initial reactant rotational states. It has been suggested⁵ that this may be an important aspect of the dynamics of reactions producing polyatomic products. It appears that there may be a direct correlation between rotational motion of the reactants and the bending vibration of the product. An important dynamical problem may well be *not only* the product vibrational state distribution of Reaction (1) but also its dependence on the initial rotational states of the reactants. The implications of this preliminary investigation indicate that HCN bending vibrations are preferentially populated in Reaction (1). The potential energy surface governing Reaction (1) and the $\text{CN} + \text{O}_2$ reaction are likely to have many features in common although the exothermicity of the latter reaction is only half that of the former. Both reactions proceed with little or no activation barrier and produce vibrationally excited products. This indicates that the surface is of the "attractive" type with the transition state for reaction located early on the reactant side.

7. CONCLUSION

Preliminary results have been presented for the product HCN vibrational state distribution from Reaction (1). Only a very small fraction of the HCN molecules are produced in the $(0,0,v_3)$ manifold and the ground state $(0,0,0)$ is not produced at all. It is speculated that a substantial fraction of the product HCN molecules are produced in bending vibrational levels. Some evidence for the vibrational adiabaticity of the CN reactant vibration was presented but further clarification of this effect is needed.

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