Final Report

LABORATORY STUDIES OF LOW TEMPERATURE RATE COEFFICIENTS: THE ATMOSPHERIC CHEMISTRY OF THE OUTER PLANETS AND TITAN

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Summary

Laboratory measurements have been carried out with the NASA grant No. NAG5-4314 (January 1, 1997 - December 31, 1999) to determine low temperature chemical rate coefficients of ethynyl radical (C_2H) for the atmospheres of the outer planets and their satellites. This effort is directly related to the Cassini mission which will explore Saturn and Titan. A laser-based photolysis/infrared laser probe setup was used to measure the temperature dependence of kinetic rate coefficients from ≈ 150 to 350 K for C_2H radicals with H_2, C_2H_2, CH_4, CD_4, C_2H_4, C_2H_6, C_3H_8, n-C_4H_{10}, i-C_4H_{10}, neo-C_5H_{12}, C_3H_4 (methylacetylene and allene), HCN, and CH_3CN. The results revealed discrepancies of an order of magnitude or more compared with the low temperature rate coefficients used in present models. A new Laval nozzle, low Mach number supersonic expansion kinetics apparatus has been constructed, resulting in the first measurements of neutral C_2H radical kinetics at 90 K and permitting studies on condensable gases with insufficient vapor pressure at low temperatures. New studies of C_2H with acetylene have been completed.

Final Progress Report NAG5-4314

This program involves the measurement of low temperature rate coefficients for neutral radical reactions that are important in models of the planetary atmospheres of Saturn, Titan, and Jupiter. A key goal is to obtain benchmark sets of rate coefficients for a number of different chemistries that will be needed to help analyze the results of the Cassini/Huygens mission; the results are also immediately applicable to recent Galileo measurements and models for Jupiter. Research under the three-year grant NAG5-4314, "Laboratory Studies of Low Temperature Rate Coefficients: The Atmospheric Chemistry of the Outer Planets," provided an outstanding number of new measurements of kinetic rate coefficients for C_2H radical reactions with many of the relevant saturated and unsaturated hydrocarbon molecules. Using a laser pump/probe apparatus, most of these measurements were made in a low temperature flow cell over the temperature range from 300-360 K down to 150-170 K. Through a major equipment grant, a conceptually different Laval nozzle apparatus was designed and constructed during the previous grant period to achieve much lower temperatures, which is especially important to study condensable gases, i.e. gases with insufficient vapor pressures at low temperatures. The first measurements of rate constants for hydrocarbon radical reactions down to 90 K were achieved with this apparatus. Below is a description of the two experimental techniques used and the recent results and their interpretations.

Laser Pump/Probe Results of Low Temperature Kinetics

The laser pump/probe apparatus consists of an ultraviolet laser for photolysis and an infrared probe laser for transient absorption of the C_2H radicals. The rate measurements are carried out as a function of temperature in a transverse flow cell designed specifically for achieving low temperatures.

In a typical experiment, a 193 nm argon fluoride pulsed excimer laser is used to photolyze a suitable precursor molecule (acetylene, C_2H_2) to produce C_2H, and a high resolution, tunable infrared F-center laser probes the transient concentrations of the radical species directly in absorption to extract the kinetic rate coefficients. The experiment involves flowing a mixture of a precursor molecule, such as C_2H_2 and a reactant, such as H_2, methane (CH_4), acetylene, or larger hydrocarbons in a rare gas buffer through the 100 cm long cell. The photolysis beam and probe laser beam (multipassed to increase the absorbance) are overlapped over the length of the cell by means of dichroic mirrors which reflect one wavelength and are transparent to the other. The cell is operated with various cooling fluids and a low temperature circulating pump to achieve temperatures routinely down to 150 K. The kinetics are carried out in the pseudo-first order regime so that the observed time decays of the radical signals are related to the first order removal rates of the radical species.

In Table 1 below, our measured rate coefficients for the C_2H + hydrocarbon reactions and cyanide compounds are summarized. The measurements are made over a range of temperatures, but only the lowest temperatures are shown in the table. New measurements on the larger hydrocarbon species (C_3H_8, $i\text{-}C_4H_{10}$, $n\text{-}C_4H_{10}$, $neo\text{-}C_5H_{12}$, CH_3CCH, and CH_2CCH_2) and the coupling reactions with nitrogen compounds (HCN, CH_3CN) were the focus of the experiments in the last three years. In the table, the measurements are compared with those values currently used in many of the atmospheric models (Gladstone *et al.* 1996). In addition to the Gladstone *et al.*

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(1996) model for the atmosphere of Jupiter, other recent major models for Titan's atmosphere are given by Toublanc *et al.* (1995) and Lara *et al.* (1996). These add to the already existing models of Yung *et al.* (1984, 1987) developed for Titan. While there are some differences in the rate coefficient values used in these models, a detailed assessment of the rate coefficients used in each model is not considered here, but discussions are included in each of our publications on the specific reactions.

As can be seen from the table, there are considerable discrepancies (30% to an order of magnitude) between the accurately determined experimental values and many of the quantities presently used in the models. In some cases the models are not that sensitive to a particular rate and the use of a slightly different number is not a problem. In others, the models use only room temperature values. In still others, the use of the new determinations would cause the concentrations of some species to be altered even further from expectations. For example, in Gladstone *et al.* (1996) the rate coefficients of key C_2H reactions are adjusted to maximize the ethane to acetylene ratio for Jupiter using only older literature values, rather than the newer determinations, which would make the agreement even worse. This practice could result in

Table 1 Some low temperature rate coefficients measured in this work compared to values presently used in models.[a]

Reaction	Temperature	Measured ($cm^3 \, s^{-1}$)	Gladstone *et al.* 1996
$C_2H + H_2$	178 K	5.0×10^{-14}	1.7×10^{-14}
$C_2H + CH_4$	154 K	5.5×10^{-13}	1.8×10^{-12}
$C_2H + C_2H_2$	143 K	1.9×10^{-10}	1.5×10^{-10}
$C_2H + C_2H_6$	153 K	3.3×10^{-11}	2.1×10^{-11}
$C_2H + C_2H_4$	150 K	1.4×10^{-10}	2.0×10^{-11}
$C_2H + C_3H_8$	180 K	1.1×10^{-10}	1.4×10^{-11}
$C_2H + i\text{-}C_4H_{10}$	177 K	1.0×10^{-10}	1.4×10^{-11}
$C_2H + n\text{-}C_4H_{10}$	176 K	1.6×10^{-10}	1.4×10^{-11}
$C_2H + neo\text{-}C_5H_{12}$	181 K	1.3×10^{-10}	none
$C_2H + CH_3CCH$	155 K	2.4×10^{-10}	none
$C_2H + CH_2CCH_2$	159 K	2.4×10^{-10}	none
$C_2H + HCN$	297 K	3.9×10^{-13}	2.2×10^{-12}
$C_2H + CH_3CN$	262 K	1.0×10^{-12}	none

[a]No error bars are shown, see publications. Most measurements are carried out over a wide temperature range, from the lowest value indicated in the table to 300 K or 360 K, and a complete temperature fit is formulated for each reaction. Each measurement consists of many data runs.

important pathways being overlooked. In addition, sometimes the models may have relied too

heavily on the older Voyager data for species concentrations, resulting in inappropriate adjustments to the model parameters.

Summary of Results

The results for the reactions of C_2H with H_2 (Opansky and Leone 1996a), CH_4 (Opansky and Leone 1996b), C_2H_2 (Pedersen *et al.* 1993, Opansky and Leone 1996b), C_2H_4 (Opansky and Leone 1996a), C_2H_6 (Opansky and Leone 1996a), and O_2 (Opansky *et al.* 1993) were discussed in detail in the previous proposal. We briefly discuss below the interpretation of some of the more recent results in the table above.

$C_2H + C_3H_8$, n-C_4H_{10}, i-C_4H_{10}, and neo-C_5H_{12}

The reactions of C_2H with large saturated and unsaturated hydrocarbons are not well characterized. Gladstone *et al.* (1996) urged that there be more rate determinations of radicals with C_3 and larger hydrocarbon species, and they indicated that these rates will be crucial to understand the carbon partitioning on Jupiter. One of the difficulties with studies of these species is that the gases start to be condensable at low temperatures. Our results for C_2H with C_3H_8, n-C_4H_{10}, i-C_4H_{10}, and neo-C_5H_{12} (Hoobler *et al.* 1997) are the only absolute rate coefficient determinations ever reported for these processes and the measurements are successfully made down to 150-180 K in the flow cell, depending on species. The measurements show that the C_2H reactions with the larger hydrocarbons have very rapid rates, much larger than the estimates used in the models (Table 1). In some models these reactions are not yet included.

The results for propane are nearly independent of temperature, whereas for *n*-butane, isobutane, and neopentane the temperature dependencies are negative (Hoobler *et al.* 1997), indicating that the rates are increasing with decreasing temperature. The negative temperature dependencies stress the need for the Laval nozzle measurements, which will be carried out at even lower temperatures and are discussed later. The values presently used in the models of the planetary atmospheres are in error by nearly an order of magnitude, even before extrapolation to lower temperatures, and at the lowest temperatures of 70 K on Titan, the actual rate coefficients may differ even more. For these reactions, the role of possible long-lived collision complexes must be recognized in the dynamical mechanisms of the reactions. These reactions are essential to the understanding of the synthesis of larger molecules in the planetary atmospheres, since they create larger radicals which can then recombine, affecting the ratios of various hydrocarbons in the atmosphere. Thus the formation of adduct species, which could be important products of these reactions, will also need to be determined.

$C_2H + CH_3CCH$ and CH_2CCH_2

The reactions of C_2H with methylacetylene (CH_3CCH) and allene (CH_2CCH_2) were identified by Gladstone *et al.* (1996) as key processes involving C_3 species that need to be included in the atmospheric models, but which have not been incorporated to date. Reactions with other species that have similar concentrations, however, such as diacetylene, cyanoacetylene, and cyanogen, have already been included. Our results are the first determinations of reaction rate coefficients for C_2H with C_3H_4 molecules (Hoobler and Leone 1999). Both reactions are fast, and

the temperature dependencies are either flat or slightly negative, predicting significantly faster reactions as the temperature becomes lower. At the lowest temperatures studied, 155 K, condensation of the C_3H_4 species becomes a problem, and thus an observed leveling off of the rate constants below 200 K is most likely due to condensation loss of the reactants. The rate coefficients under the conditions of the planetary atmospheres are likely to be even greater.

These reactions have many possible products. For example, the reaction of C_2H with methylacetylene can form five possible products: $C_2H_2 + CH_2CCH$, $C_2H_2 + CH_3CC$, $C_4H_2 + CH_3$, $C_5H_4 + H$, and C_5H_5. Some of the products involve abstraction processes and others involve adduct formation. In future work it will be important to determine which of the various product species are formed and their branching ratios. Although some aspects of the photochemistry of methylacetylene and allene have been included in the models of the planetary atmospheres of Titan and Jupiter, these processes have often emphasized only photolysis, reactions with H atoms, and condensation. As the models become more complete, the reactions of C_3H_4 species with C_2H can now be included with accurate rate coefficients as well.

C_2H + HCN and CH_3CN

Studies of the reaction of C_2H with HCN and CH_3CN are particularly troublesome because of the ease of condensation (low vapor pressure) of these nitrogen-containing compounds at low temperatures. Thus our measurements (Hoobler and Leone 1997) with the flow cell apparatus were limited to a very narrow temperature range of 262-360 K. In addition, while some estimates suggested that these reactions might be rapid, in fact we find the reactions are extremely slow, have a significant barrier, and are therefore even more difficult to measure. Our own *ab initio* calculations show that the lowest-barrier transition state of the C_2H + HCN reaction leads to HC_3N + H products, formed via an addition-elimination mechanism; the calculations confirm that there is a high barrier, which is the reason that the reaction is slow.

In the current atmospheric models of Titan (Lara *et al.* 1996), the rate coefficient assumed for the reaction of C_2H + HCN $\rightarrow$ HC_3N + H and the eddy diffusion coefficient are critical features in obtaining the abundance of HC_3N. The much smaller value of the rate coefficient obtained here compared to that used by Lara *et al.* (more than a factor of 30 for the room temperature value and 200 times smaller when the experimental temperature dependence is extrapolated to 170 K) has significant impact on the modeled HC_3N distribution and the discrepancies with Voyager/IRIS measurements. The model (Lara *et al.* 1996) predicts vertical profiles for the HC_3N mixing ratio that are too high by nearly two orders of magnitude. Both reactions decrease substantially with decreasing temperature, suggesting that at the lowest temperatures on Titan, these reactions will be very slow indeed.

Other models utilize different eddy diffusion coefficients, photolysis production rates, and assumptions about the neutral radical rate coefficients. Therefore it is not straightforward to compare resulting numbers from each model without detailed knowledge of the contributing and canceling factors. A detailed analysis of the parameters for several models is contained in Hoobler and Leone (1997). However, it is valuable to present the results of a reassessment of the predictions made by Hoobler and Leone (1997) for the HC_3N production rates. This reassessment is based on just the changes in two experimental rate coefficients, for the C_2H + HCN reaction

measured here and the CN + C_2H_2 reaction measured by Sims *et al.* (1993). The results in Table 2 reveal how dramatic the affect is on the calculated HC_3N species.

Table 2 Reassessment of the Production Rates for HC_3N Species Compared to Models.[a]

Reaction Path	Reassessment	Yung *et al.* 1984	Toublanc *et al.* 1995	Lara *et al.* 1996
$C_2H + HCN \rightarrow$ $HC_3N + H$	0.008[b]	0.3	0.5	0.3
$CN + C_2H_2 \rightarrow$ $HC_3N + H$	14[c]	2	75	3600

[a] In molecules cm^{-3} s^{-1}
[b] Using k=5 x 10^{-14} based on extrapolation to 170 K.
[c] Using k=4 x 10^{-10} from Sims *et al.* 1993.

Laval Nozzle Apparatus for Low Temperature Kinetics

As noted above, many of the reactions of interest for the outer planets occur at temperatures down to 70 K, for example on Titan. Because of the low vapor pressure of many reagents, the gases are condensable at low temperatures, and the kinetic determinations of most reactions can only be measured in flow cells down to 150 K or, in many cases, only at 300 K. As shown in our studies, there are often dramatic changes in the rate coefficients at lower temperatures, and it is often not possible to predict whether the rates will increase, decrease, or remain the same upon lowering the temperature.

An important instrumental development was made in this grant period with the support of a major equipment grant from NASA (Lee, Hoobler, and Leone 2000). We constructed a low Mach number supersonic Laval nozzle expansion as a new apparatus for making neutral kinetics measurements at temperatures much lower than possible with a flow cell. The Laval nozzle expansion produces a long (20 cm) region of uniform low-temperature gas, which can be used for accurate kinetics measurements down to 20 K (Sims *et al.* 1992, Hawley *et al.* 1990, Smith and Hawley 1992, Sims *et al.* 1993, Sims *et al.* 1994, Atkinson and Smith 1994, Atkinson and Smith 1995). The Laval nozzle expansion creates the constant low temperature zone over which the reactions can proceed without the interference of walls. The continuous flow Laval nozzle method requires an enormous pumping system, which is beyond the limits of reasonable laboratory size and expense. However, the method of Atkinson and Smith uses a pulsed valve source for the supersonic Laval nozzle expansion and this method was adapted in our laboratory with rather modest pumps and cost. We also developed a rather general single photon laser ionization scheme for detection of radical and neutral species; this method uses the 9th harmonic of the Nd:YAG laser at 118 nm (10.5 eV per photon), which had already been demonstrated for polyacetylene species (Bandy *et al.* 1992, Frost *et al.* 1995) and used in our laboratory for molecular beam epitaxy species (Strupp *et al.* 1993).

Figure 1 shows the Laval nozzle apparatus constructed in our laboratory. It consists of a pulsed valve and a shaped Laval nozzle to produce a uniform low temperature gas flow, a 193 nm photolysis laser to generate the radical of interest, a skimmer to sample the gas stream, impact pressure transducers to characterize the beam, the 118 nm ionization laser, and a time-of-flight mass spectrometer. For kinetics the nozzles are shaped to produce a uniform density of low temperature gas over a long path length.
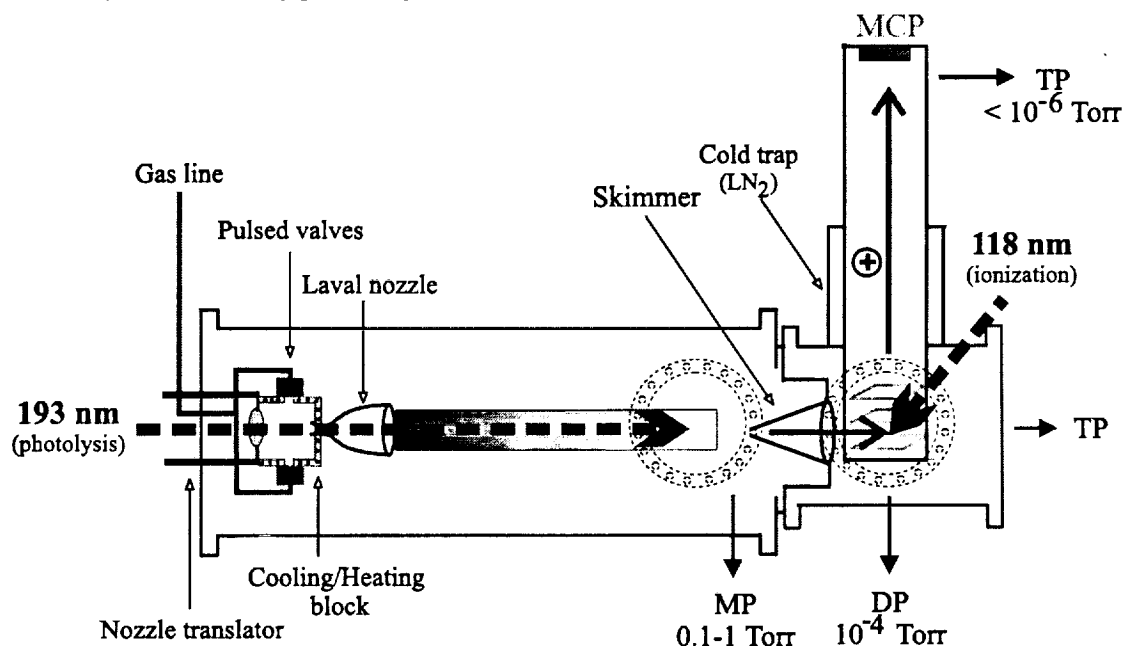

Figure 1   Pulsed Laval nozzle apparatus for low temperature kinetics.

A uniform density of radicals is produced by laser initiation coaxially along the path of the expansion using a pulsed excimer laser at 193 nm. The pulsed laser ionization probe is used to detect the products either as a function of distance along the expansion, a function of concentration of the reactant, or by precision time delays between the two pulses. We have provision to substitute a resonantly enhanced multiphoton ionization (REMPI) process to probe selectively an individual radical species of interest. The ions are sampled from the flow with a skimmer and extracted into the entrance of a differentially pumped time-of-flight mass spectrometer. The laser ionization time-of-flight mass spectrometer provides a very general method of detection for both reactants and many product species. The main criterion is that the ionization potential of the species is lower than 10.5 eV. By addition of reactive reagents into the expansion gas and accurate calibration of the flow density, the change in radical concentration as a function of distance or time delay is used to measure the reaction rate constant under pseudo first order conditions. The reaction distance is readily varied by changing the distance of the probe laser from the nozzle exit, and the timing between the two lasers sets accurately the time for the reaction to proceed. Using a variety of nozzles, and with heating and cooling of the nozzle body, expansions can be achieved with temperatures ranging from 70 K to 300 K.

A Laval nozzle is a converging-diverging channel for obtaining prescribed expansions.

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The first part of the Laval nozzle is a short convergent section where the flow begins to accelerate from near zero net hydrodynamic velocity in the stagnation region. At the throat where the nozzle diameter is a minimum, the flow reaches Mach 1. Following the throat, given a sufficient pressure drop across the nozzle, supersonic flow is achieved in the divergent region. In the nozzle design, accomplished with codes provided by M. Smith at Arizona, the radius and slope at the throat must be carefully matched to the beginning of the divergent section, so that shock waves do not occur. A slip gas is added around the expansion to provide a constant stagnant gas pressure at the walls and collimate the gas flow.

Figure 2 shows the result of impact pressure transducer measurements of the beam from one of the Laval nozzles constructed for these studies. This particular nozzle was designed to operate at Mach 3, and it was found to produce Mach 3.35 with a uniform temperature in the gas flow of 89 ± 4 K at a pressure of 0.2 Torr. In the figure the excellent uniformity of the expansion and minimal spreading of the beam can be seen.

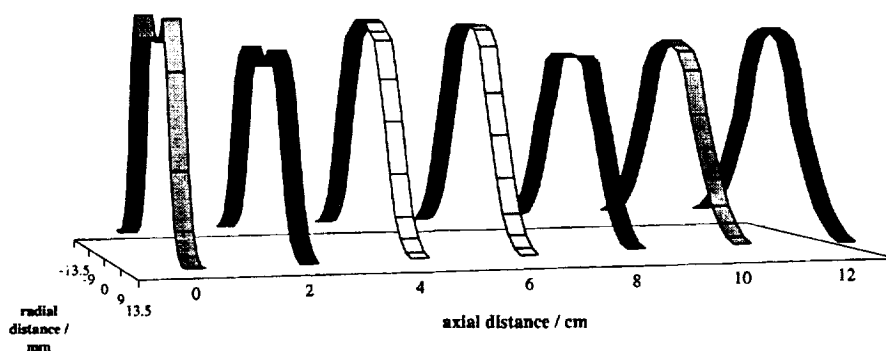**Impact Pressure Map of Mach 3.4 N_2 Flow**

Fig. 2 Impact pressure transducer measurements of the Laval nozzle output as a function of distance downstream of the flow.

A typical experiment is performed in the following manner. The photolytic precursor gas for the radical of interest, the desired reactant gas, and a carrier gas are admitted by the pulsed valve for a 5 ms duration. The supersonic expansion forms and becomes uniform. At an appropriate time after the uniform expansion characteristics have been achieved, the pulsed excimer laser is pulsed coaxially along the expansion to prepare a uniform radical density by photolysis of the precursor. The radicals begin to react with the desired reagent. At a measured time delay and given distance in the flow stream after the photolysis pulse, the probe laser is pulsed to interrogate the remaining radical density by producing ions. The integrated ion signals are collected by the TOF-MS and measured with the data acquisition. Measurements can be taken either at various distances in the expansion at a fixed time delay or at various time delays at a fixed distance to

extract the rate information, as a function of reactant concentration. Impact pressure transducers (Fig. 2 above) are used to characterize the nozzle expansion Mach number and, from that determination, the density and then the temperature are computed (Atkinson and Smith 1995). These temperatures can be checked by measuring a rotational population distribution by REMPI for a typical gas like NO. Under nonreactive conditions, the signals from the probe laser can also be used to determine the uniformity of the radical density along the expansion length. The temperature is varied by using a variety of removable nozzles and by heating and cooling the nozzle body with a circulating fluid.

In the experiments the gas pulse from the Laval nozzle is 5 ms long, and the 20 ns excimer laser pulse irradiates only a very small slug of gas along the length of the entire gas pulse. In Fig. 3, timing diagram depicts an actual gas pulse, the small slug of gas irradiated by the excimer laser pulse at a time of 3 ms, and an expanded view of the portion of the gas pulse that is photolyzed,
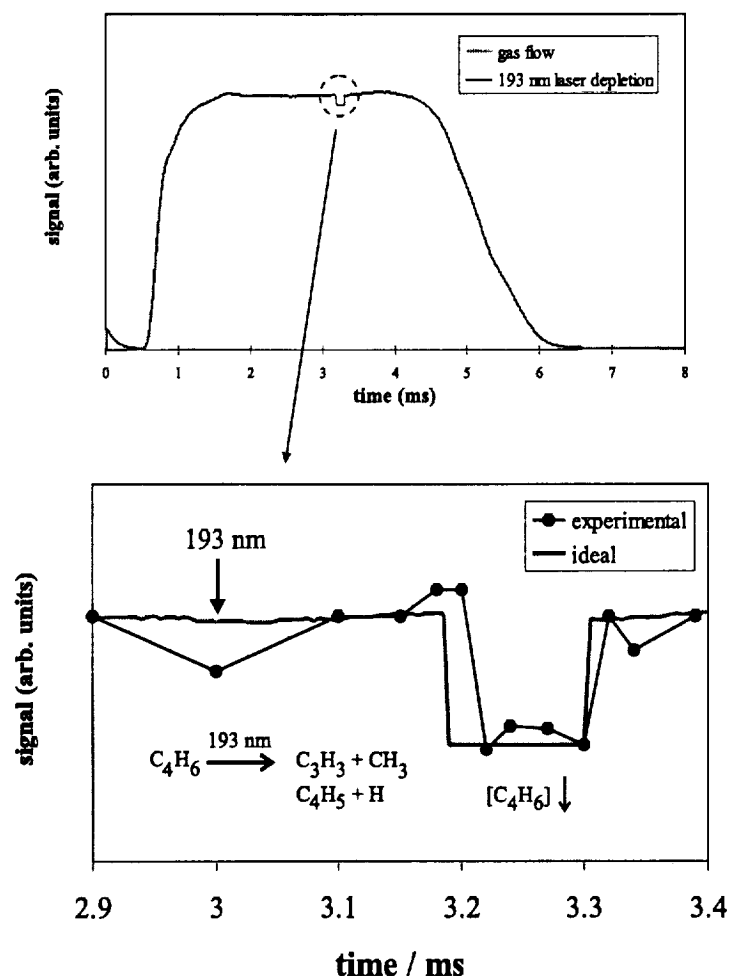
Figure 3 Timing diagram with measured data for the Laval nozzle gas pulse and the excimer photolysis pulse, detected by the 118 nm laser.

showing the ideal profile of depletion that would be created by the excimer pulse and the actual depletion measured by the 118 nm probe laser. In this figure, C_4H_6 gas is photolyzed by the excimer laser, and the depletion of the C_4H_6 is detected by the 118 nm ionizing pulse as a function of time delay between the 193 nm excimer and the 118 nm ionizing laser. The excellent response time of the experimental data, for the depletion signal and its transport through the skimmer and mass spectrometer, is critical for good kinetics, which otherwise could blur the kinetic timing. The time between the 193 nm photolysis pulse indicated on the figure and the first arrival of the depletion signal is simply due to the transit time of the gases from the probe laser through the skimmer and into the mass spectrometer detector (at Mach 3.35, the velocity is 650 m s^{-1}).

With the Laval nozzle apparatus, we have been able to make the first measurements of the reaction of C_2H with C_2H_2 at 90 K (Lee, *et al.*. 2000). In Fig. 4, the C_2H radical reaction is monitored through the C_4H_2 product, which is detected as a function of C_2H_2 reagent concentrations to extract the kinetic rate constant. The results are obtained from data runs that produce ≥20 counts of C_4H_2 signal each, and multiple data runs at two different C_2H_2 densities are averaged to obtain the rate constant. The results show that the trend of the rate coefficients is followed to lower temperature, namely that the reaction rate constant continues to increase with decreasing temperature. In fact the change from 150 K to 90 K is significant, amounting to a 20% increase. These are the first measurements of any C_2H radical reaction at temperatures down to 90 K (k = (2.3±0.4) x 10^{-10} cm^3 molecule^{-1} s^{-1}), marking a significant breakthrough in the ability to measure neutral reaction processes of relevance to the atmosphere of Titan and the outer planets.
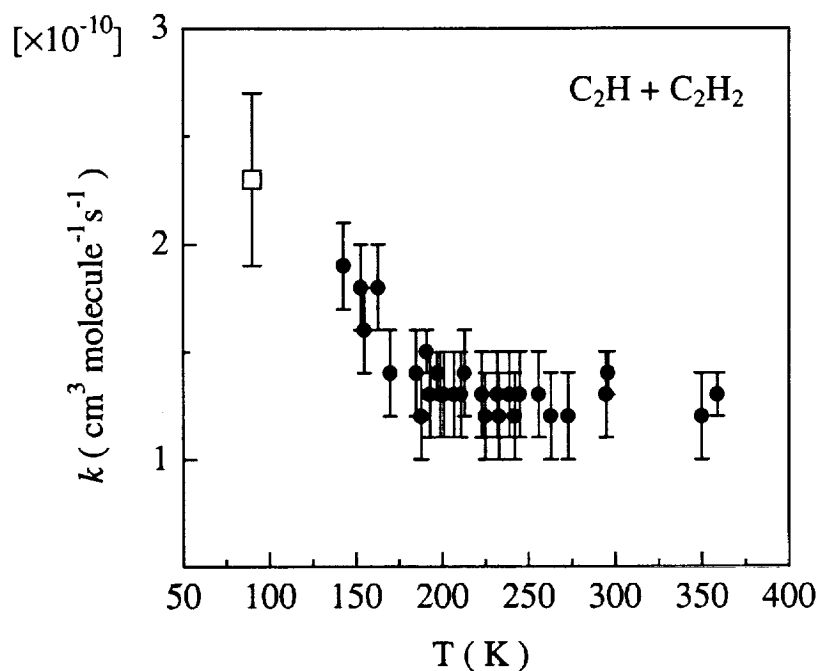

Fig. 4 Rate constant vs. temperature for the $C_2H + C_2H_2$ reaction. The new result at 90 K is obtained with the Laval nozzle apparatus.

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In a preliminary study, the reaction of C_2H with O_2 was examined at 90 K by detecting the HCCO product (ionization potential 9.5 eV) by laser ionization. We were also able to detect the CO_2 product, even though the ionization potential of this species is 13.8 eV, too high for a single photon process, but possibly by a multiphoton ionization process involving 118 nm and 355 nm photons. The importance of this result is that it demonstrates the detection of multiple products of a reaction with this apparatus. Work is in progress to measure the rate coefficients of this reaction at several temperatures, as well as the $C_2H + C_3H_4$ reactions (allene and methylacetylene) and to determine more about the product branching in these reactions at 90 K.

Publications During Grant Period

Hoobler, R. J., Opansky, B. J., and Leone S. R., "Low-Temperature Rate Coefficients for Reactions of Ethynyl Radical (C_2H) with Propane, Isobutane, n-Butane, and Neopentane," *J. Phys. Chem.* 100, 1338 (1997).

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