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"Laboratory Studies of Low Temperature Rate Coefficients:
The Atmospheric Chemistry of the Outer Planets"

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Introduction

The purpose of the project is to perform laboratory measurements of reaction rate coefficients at low temperature. The reactions and temperatures of interest are those that are important in the chemistry of the hydrocarbon rich atmospheres of the outer planets and their satellites. In this stage of the study we are investigating reactions of ethynyl radicals, C_2H, with acetylene (C_2H_2), methane (CH_4), and hydrogen (H_2).

In the previous status report from January 24, 1992, we reported on the development of the experimental apparatus and the first, preliminary data for the $C_2H + C_2H_2$ reaction.

Experimental Apparatus

A schematic of the present experimental setup is shown in figure 1. Briefly, the ethynyl radicals are generated photolytically using a pulsed 193.3 nm excimer laser, and a high resolution, tunable infrared color-center laser probes the transient concentrations of the C_2H radicals directly in absorption to extract the kinetic rate coefficients.

The kinetic experiments are carried out in a cylindrical flow cell, of length 100 cm and a diameter of 2.5 cm, where the two laser beams are overlapped over the full length of the cell. Figure 2 shows the details of the flow cell which has been designed for this work. The cell is made of quartz and is constructed with a series

of transverse inlets and pump-outs. This transverse arrangement allows rapid removal of the photolysis products from the probe volume. In the experiment a mixture of a precursor molecule, a reactant, a helium buffer gas and a vibrational relaxer is flowed through the cell. The helium buffer ensures translational relaxation and a rapid equilibrium with the temperature of the walls of the flow cell. Sulphur hexafluoride (SF_6) was used at the higher temperatures as the vibrational relaxer. However, because of the possibility of condensation we use carbon tetrafluoride (CF_4) as a vibrational relaxer at the lowest temperatures. CF_4 has the advantage of having a higher vapor pressure but is less efficient in quenching the excited C_2H radicals compared to SF_6.

The cell is surrounded by an insulated jacket into which a coolant is flowed. We have initially used nitrogen as the coolant by first flowing it through a copper coil submerged in a liquid nitrogen dewar. The temperature of the nitrogen gas and thus the reaction cell was then controlled by adjusting the nitrogen gas flow. A type K thermocouple probe samples the gas temperature inside the cell and the pressure is measured with a 100 Torr MKS Baratron absolute transducer.

This cooling method was, however, found not to produce a completely uniform temperature in the cell, and in some cases parts of the cell could become so cold that condensation of the gas mixture would occur. Several different ways of distributing the cooled nitrogen in the outer jacket of the cell were tried without evading the problem of cold spots in the cell. The problem was first solved by filling the jacket with an ethanol/liquid nitrogen slush, and kinetic data were then taken as the slush was slowly warming up. A problem with this method was that the slush would warm up faster near the ends of the cell than around its center. Finally the uniform cooling problem has been completely resolved by using an alcohol coolant which is circulated through the jacket using a small pump (Micropump Corp.).

The alcohol (with pentane or ethanol/methanol mixtures) is cooled by pumping it through the cell in series with a copper coil submerged in a slush. A

very uniform temperature (±1 K) of the coolant has been obtained this way and also a good correspondence between the temperature of the coolant and the flowing gas mixture. The coolant temperature and thus the temperature of the gas mixture can be easily adjusted by adding small amounts of liquid nitrogen to the slush. The O-rings used in the Micropump restrict the temperature of the coolant to values above 210 K, where the alcohol starts to leak from the pump. We have therefore recently purchased a centrifugal low temperature pump (FTS systems) which can operate from 125 K to 375 K. The pump will be used together with a new quartz flow cell which is near completion and is equipped with a coolant inlet at one end and an outlet at the other end of the outer jacket. Insulated silicone tubing will be used to transport the coolant between a reservoir in series with the centrifugal pump, a dewar and the cell. The cell has a gas flow arrangement similar to the present flow cell but has an additional four thermocouple inlets distributed over the length of the cell and will thus allow us to obtain information about possible temperature gradients over the length of the cell.

The present cell will be modified to be used with the same cooling arrangement and the two cells can then easily be interchanged. This will reduce the experimental dead time when the cell has to be taken out for a thorough cleaning of photolysis products.

Among the experimental problems encountered was the formation of a thermal lens in the gas following photolysis. Careful alignment of the overlapping laser beams, maintaining clean excimer optics and restricting the maximum excimer pulse energy to about 70 mJ has been found to reduce the effects from thermal lensing significantly.

Finally, data transfer time from the digital oscilloscope has been greatly reduced by replacing an existing IBM XT with a new Everex Tempo 386 computer in the laboratory.

Experimental results

In the study of the $C_2H+C_2H_2$ reaction we have so far used acetylene as the C_2H precursor. All experiments were performed under pseudo-first-order conditions with $[C_2H]<<[C_2H_2]$. Figure 3 shows typical traces representing the transient C_2H population for different acetylene concentrations at a temperature of 215 K. The change in absorption of the probe beam was fit to the equation

$$I(t) = I_0 \exp(-t/\tau) + B$$

where I_0 and B are empirical detection constants. The zero on the time axis is determined by the trigger signal from the excimer beam and the start of the fitting range was chosen as three times longer than the estimated time constant for the fast initial signal rise. The random error in the extracted decay times was estimated by varying the initial fitting parameters. The inverse time decay constant $1/\tau$ is related to the $C_2H + C_2H_2$ bimolecular rate coefficient k by

$$\tau^{-1} = k_0 + k\,[C_2H_2]$$

where k_0 is the rate of loss from other processes, such as diffusion out of the probe volume and reaction with product molecules or recombination. The value of k was determined by a linear least-squares fit as shown in figure 4. The uncertainty in the acetylene concentration is calculated from the accumulated uncertainties in the instruments used for the pressure, temperature, and flow rate measurements. This uncertainty together with the uncertainty on τ is then used to calculate the resulting uncertainty on k.

From measurements with varying total pressures between 1.3 and 8 kPa we found the rate coefficient to be independent of pressure. At room temperature a value of $1.3\pm0.2 \times 10^{-10}$ cm^3 molecules^{-1} s^{-1} was obtained, which is in good agreement with recent measurements by Shin and Michael[1] and Stephens et al. [2] who found values of 1.4 and 1.5×10^{-10} cm^3 molecules^{-1} s^{-1}, respectively. These results are in disagreement with the earlier measurements of Lange and

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Wagner[3] and Laufer and Bass[4], which gave values of 0.5 and 0.3 x 10^{-10} cm^3 molecules^{-1} s^{-1}, respectively.

The rate coefficients as a function of inverse temperature are shown in figure 5, where the results of Shin and Michael[1] have been included. The two measurements at the lowest temperatures (highest 1/T values) were taken with the flowing nitrogen gas cooling and will be remeasured when the new flow cell has been installed. The temperature dependence is seen to be rather weak and has been fit with the Arrhenius expression for the rate coefficients:

$$k = A\, T^{1/2} \exp(-E_a/RT) \ .$$

From the two-parameter least-squares fit we find the values A = 6.0 x 10^{-12} cm^3 molecule^{-1} s^{-1} K$^{-1/2}$ and E_a = -0.148 kcal mol^{-1} (-52 cm^{-1}). The fit, which is shown in figure 5 as the dashed line, is seen to give a good description of the data over the whole temperature range. For comparison a fit to the data with the activation energy set to zero is also shown (solid line). It should be noted that the results in figure 5 are different from the very preliminary data presented for the temperature dependence in the previous status report, which suggested a stronger negative temperature dependence. We have reproduced the data in figure 5 in a large number of experiments under different conditions but this has not revealed the cause of the discrepancy with the first data obtained.

For measurements of reactions between C_2H and CH_4 and H_2 it was found necessary to avoid the fast reaction with the acetylene precursor. We have therefore used trifluoropropyne, CF_3C_2H, as a precursor and good C_2H signals are obtained. The gas mixing system has been extended with mass flow meters calibrated for CH_4 and H_2 and measurements of the reaction between C_2H and these gases are in progress.

An abstract with some of the results of the $C_2H + C_2H_2$ has been submitted to the 12th International Symposium on Gas Kinetics, July 19-24, in Reading, U.K., and an invitation to present the results in an oral presentation has been received. A preprint of a paper on these experiments has also been written.

References

1. Shin, K.S., and Michael, J.V., J.Phys.Chem. <u>95</u> (1991) 5864

2. Stephens, J.W., Jeffrey, L.H., Solka, H., Yan, W.-B., Curl, R.F., and Glass, G.P., J.Phys.Chem. <u>91</u> (1987) 5740

3. Lange, W., and Wagner, H.G., Ber.Bunsen-Ges. Phys.Chem. <u>79</u> (1975) 165

4. Laufer, A.H., and Bass, A.M., J.Phys.Chem. <u>83</u> (1979) 310
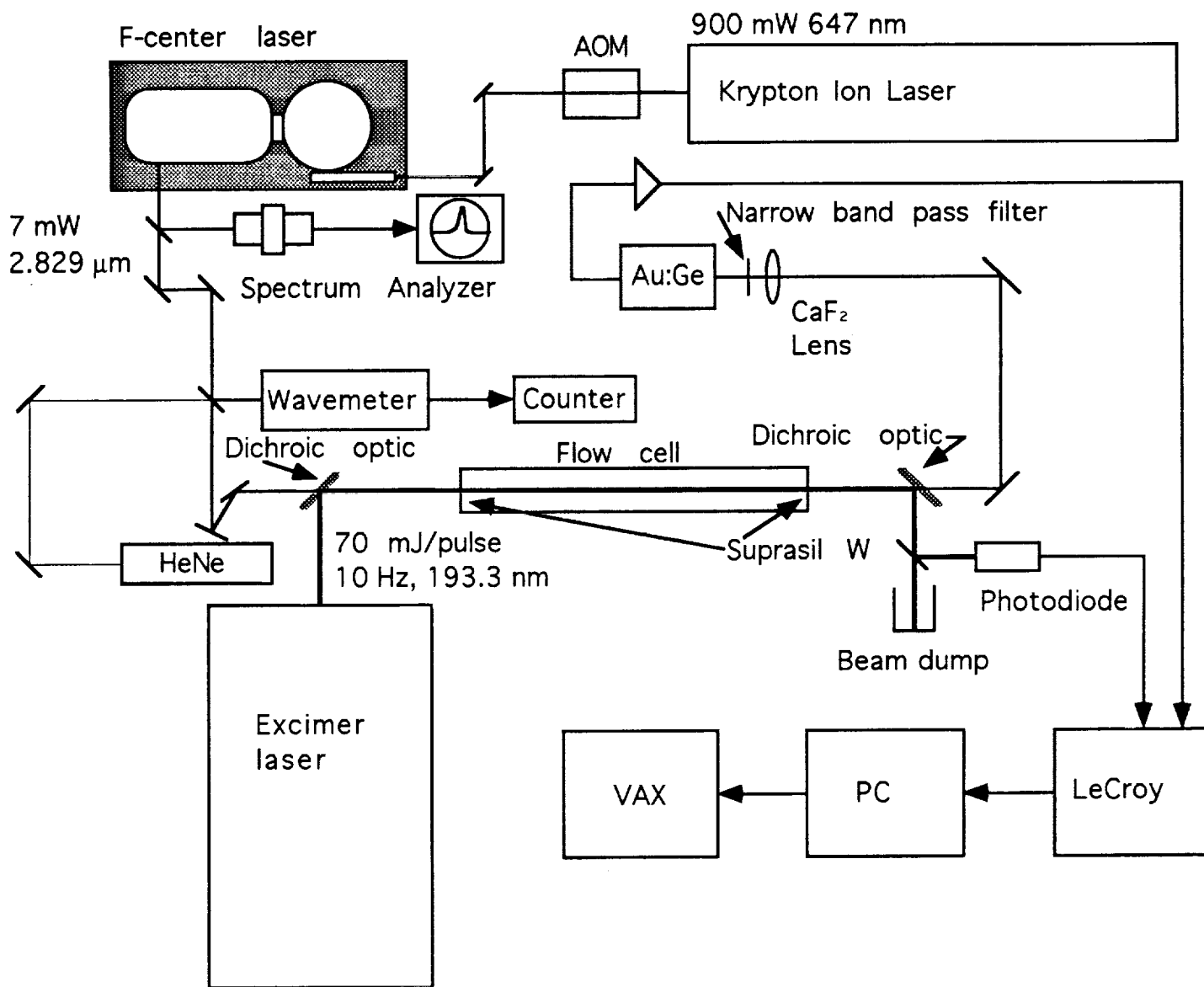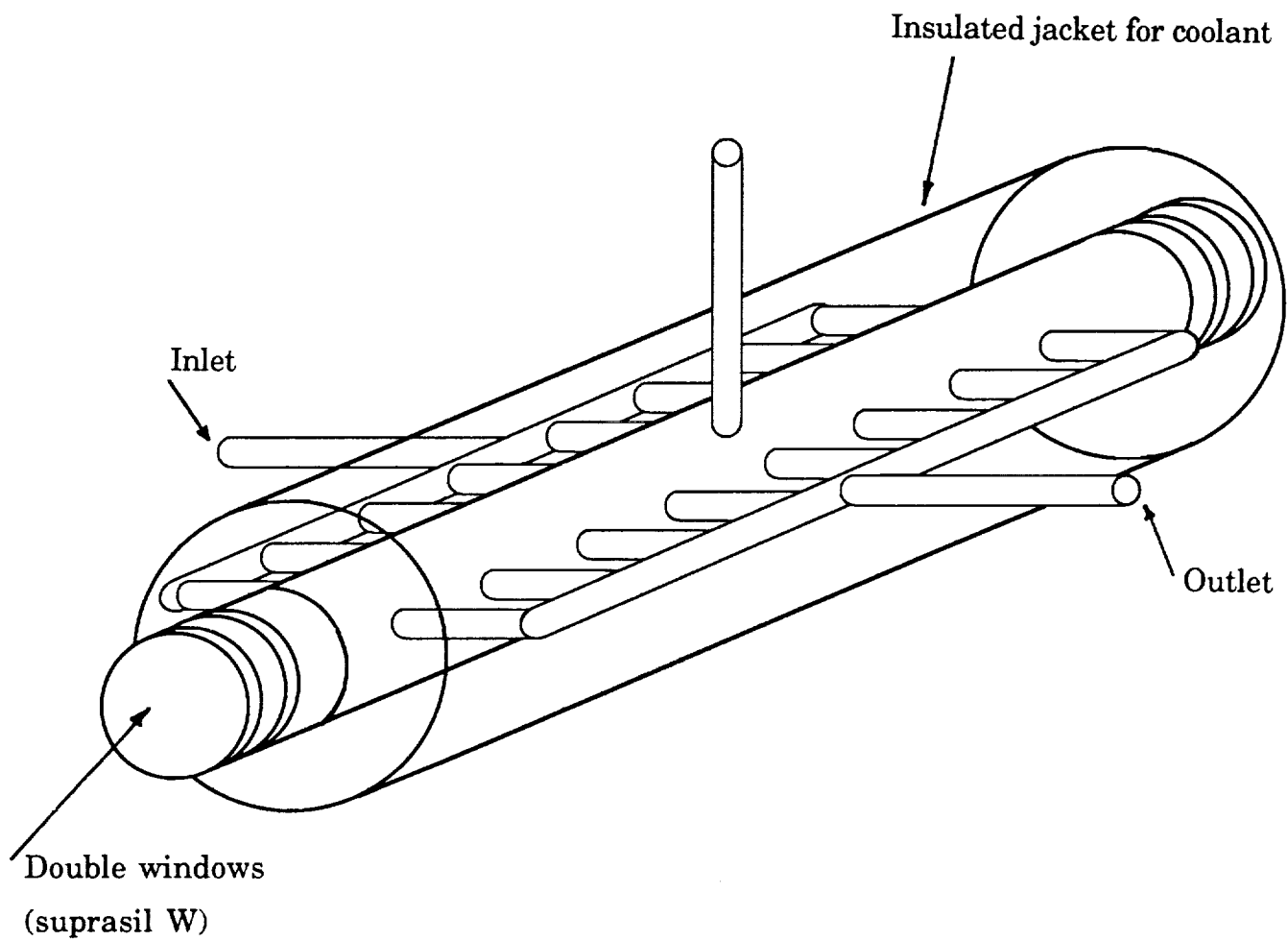
Figure 1.   Experimental setup

Insulated jacket for coolant

Inlet

Outlet

Double windows
(suprasil W)

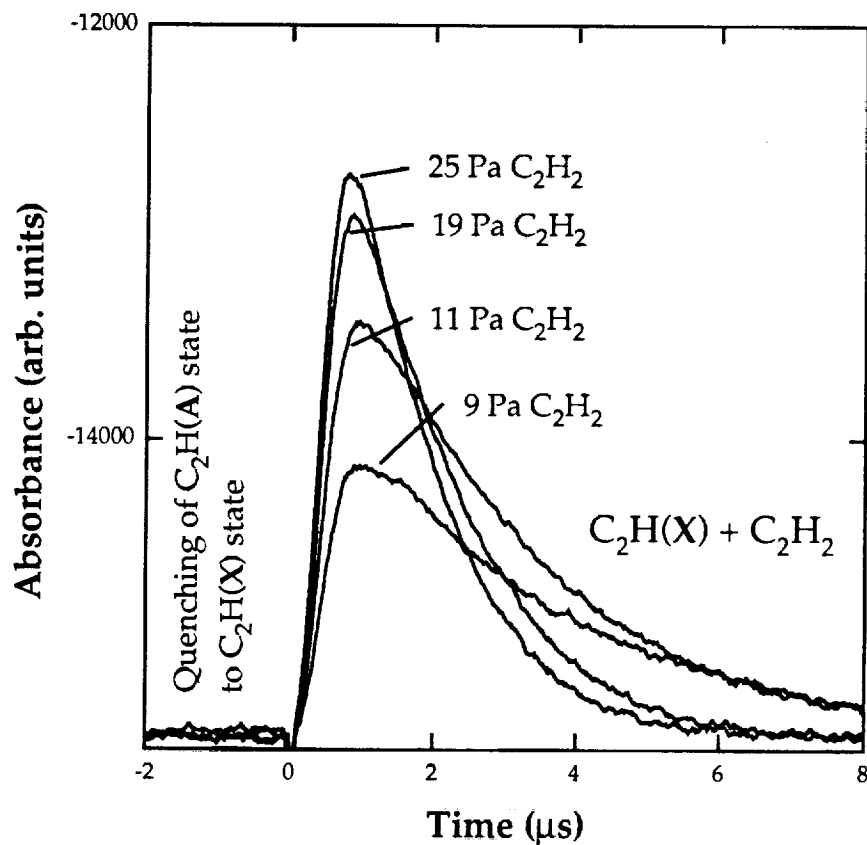Figure 2.   Diagram of the quartz low temperature flow cell.

Figure 3. Typical C_2H decay traces used for extracting the rate coefficient

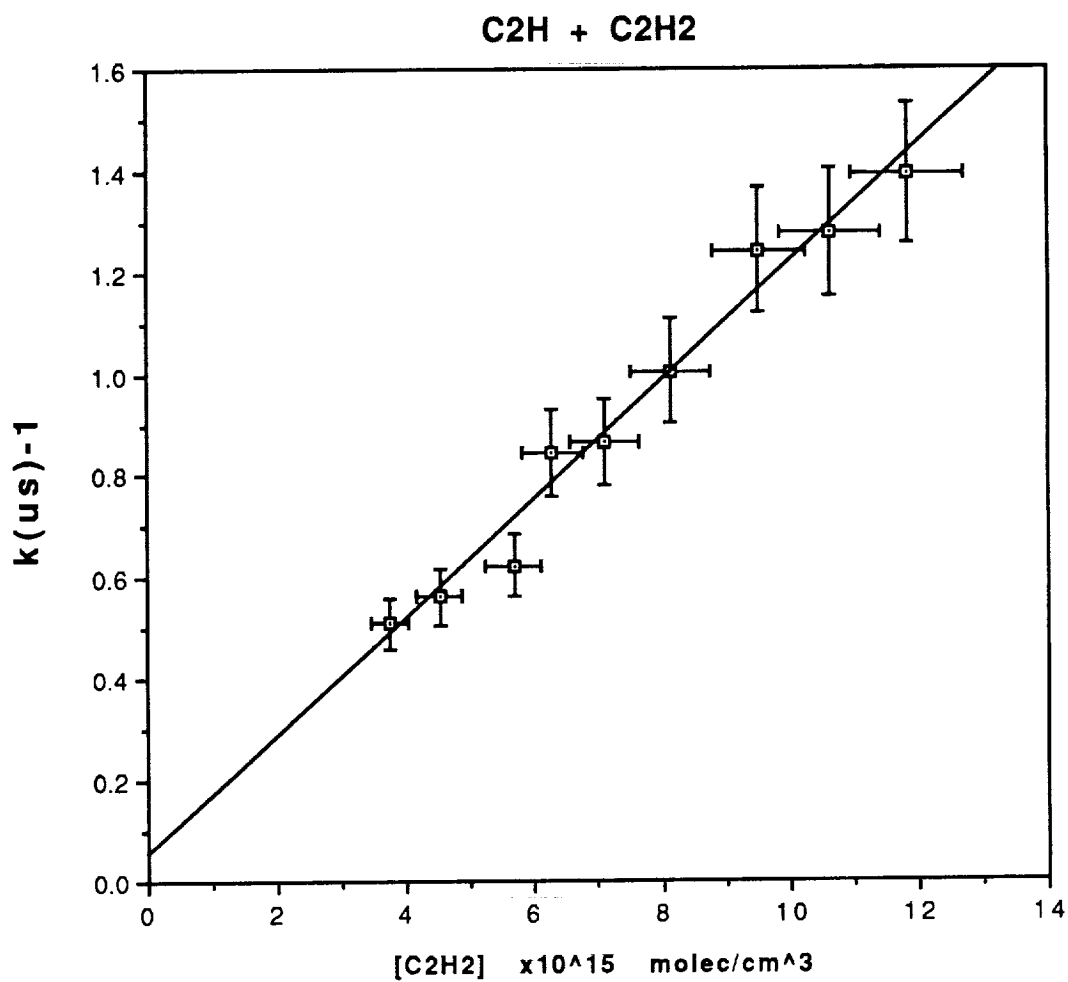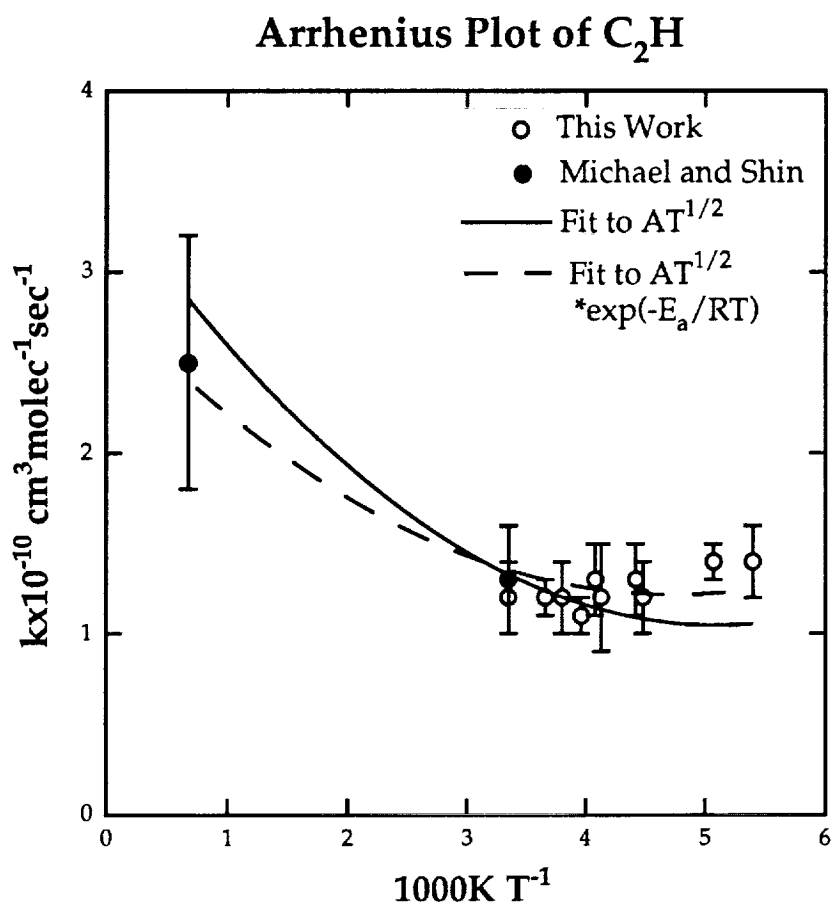Figure 4. Plot of inverse decay time constants versus C_2H_2 concentration

Arrhenius Plot of C_2H

Figure 5. Arrhenius plot of the reaction of C_2H with C_2H_2