Introduction

The objectives of NASA grant NAGW-2438 have been to measure laboratory rate coefficients for key reactions of hydrocarbon molecules and radicals at low temperatures, which are relevant to the atmospheric photochemistry of Saturn, Jupiter, and Titan. Upcoming NASA planetary missions, such as Cassini, will probe the atmosphere of Titan in more detail, offering an excellent opportunity to test kinetic models and to establish fiducial standards for using kinetic models to interpret various parameters of the outer planets. Accurate low temperature kinetic data, which are presently lacking, may require crucial revisions to the rates of formation and destruction and are of utmost importance to the success of these efforts. In this program, we have successfully investigated several key reactions of ethynyl radicals (C$_2$H) with acetylene (C$_2$H$_2$), methane (CH$_4$), and oxygen (O$_2$), down to temperatures of 170 K.

The experimental apparatus developed in our laboratory (Fig. 1) for measuring reaction kinetics at low temperatures consists of a laser photolysis/infrared probe laser setup. The rate measurements are carried out as a function of (low) temperature with a transverse flow cell designed specifically for these studies. A 193 nm argon fluoride pulsed excimer laser is used to photolyze a suitable precursor molecule, such as acetylene to produce C$_2$H, and a high resolution, tunable infrared F-center laser (2.3-3.35 μm) probes the transient concentrations of the radical species directly in absorption to extract the kinetic rate coefficients.

$C_2H + C_2H_2$

The reaction of C$_2$H with C$_2$H$_2$ is very important in the atmospheres of the outer planets. A test run for the model of Titan was performed by M. Allen of JPL; upon changing the value of the rate coefficient for the C$_2$H + C$_2$H$_2$ from 5 x 10$^{-11}$ to 1.5 x 10$^{-10}$ cm$^3$ s$^{-1}$ there is an increase in the ethane number density of a factor of ten, and acetylene increases by a factor of two. The reaction is thought to proceed by an addition-decomposition mechanism, which may be both temperature- and collision-dependent. The product diacetylene (butadiyne), C$_4$H$_2$, is a key precursor to the formation of polyacetylene hazes and ices.

The previous room temperature rate coefficient data for the C$_2$H + C$_2$H$_2$ reaction showed considerable ambiguity. Figure 2 summarizes the previous measurements as well as our new results (Pedersen et al 1993) for both room temperature and low temperature (solid circles ○). The other symbols correspond to data of Lange and Wagner 1975 (■), Laufer and Bass 1979 (□).
The solid line is calculated using simple collision theory and a steric factor of 0.3. As can be seen from the figure, almost no temperature dependence is observed for the reaction of C$_2$H + C$_2$H$_4$. Our results are the only ones that extend below room temperature. This reaction has little or no barrier to reaction, and probably involves the very short-lived C$_4$H$_3$* intermediate. We have searched for a pressure dependence to this reaction, which might indicate a collisional stabilization of C$_4$H$_3$, but none has been found.

C$_2$H + CH$_4$

The photolysis of acetylene by solar flux, which results in C$_2$H, can catalyze the dissociation of methane to form CH$_3$ (methyl radicals). The recombination of two methyl radicals produces ethane, which can then be transported downward and accumulate on the surface. Thus the reaction of C$_2$H with CH$_4$ is critically important in the planetary atmospheres. The rate coefficients for the reaction of C$_2$H + CH$_4$ at room temperature were previously reported by Laufer (1981) as 1.2 x 10$^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, Renlund et al (1981) as 4.8 x 10$^{-12}$, Lander et al (1990) as 3±0.3 x 10$^{-12}$. The first measurements in our laboratory are shown in Fig. 3. We find 2.3±0.2 x 10$^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 300 K and 1.5±0.2 x 10$^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 243 K (Opansky, Pedersen, Leone 1994).

C$_2$H + O$_2$

While the atmosphere of Titan is strongly reducing, significant amounts of CO have been detected, possibly through the introduction of cometary sources of H$_2$O. The previous room temperature data for C$_2$H + O$_2$ (Fig. 4) is scattered over an order of magnitude from 3.3 x 10$^{-12}$ to 4.2 x 10$^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Lange and Wagner 1975 (●), Renlund et al 1982 (Δ), Laufer and Lechleider 1984 (●), Stephens et al 1987 (V), Lander et al 1990 (○)). Our recent measurement (●) provides a highly accurate room temperature value of 3.3±0.3 x 10$^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Opansky, Seakins, Pedersen, Leone 1993). More importantly, the data (●) show a marked negative temperature dependence (Fig. 4).

Fig. 1 Schematic diagram of the laser photolysis, infrared probe kinetic apparatus.

Fig. 2 Kinetic rate data for C\textsubscript{2}H + C\textsubscript{2}H\textsubscript{2} (see text for details).

Fig. 3 Kinetic data for C\textsubscript{2}H + CH\textsubscript{4} (see text for values).

Fig. 4 Kinetic data for C\textsubscript{2}H + O\textsubscript{2} (see text for details).