PROGRESS REPORT
for
INFRARED ABSORPTION SPECTROSCOPY AND CHEMICAL KINETICS OF FREE RADICALS
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During the last year, three research projects have been essentially completed: a high resolution spectroscopic investigation of CH stretch of HCCN, measurement of the rate constant of the reaction between ethynyl (C_2H) radical and H_2 in the temperature region between 295 and 875 K, and measurement of the recombination rate of propargyl (CH_2CCH) at room temperature.

THE ν_1 FUNDAMENTAL OF HCCN

The CH stretch fundamental, ν_1, was observed, assigned, and analyzed. HCCN was produced by 193 nm excimer laser photolysis of dibromoacetonitrile

$$HBr_2CCN + h\nu \ (193 \text{ nm}) \rightarrow HCCN + 2Br \qquad (1)$$

and the region of the CH stretching fundamental of the ground triplet state near 3250 cm^{-1} was probed with a tunable color center laser. In addition to the CH stretching fundamental, several hot bands associated with excitation of the CH stretch from excited states of the bending vibrations were observed and the two bands associated with the lowest energy bending fundamentals, $\nu_1+\nu_5-\nu_5$ and $\nu_1+\nu_4-\nu_4$, were analyzed. From measurements of the intensity of these hot bands relative to the fundamental, the energy of ν_5 and ν_4 have been found to be 187±20 cm^{-1} and 383±20 cm^{-1} respectively. The value found for ν_5, 187±20 cm^{-1}, which corresponds to the energy of the lowest excited state involving off-axis motion, is intermediate between that expected for a normal linear molecule and that expected for a bent molecule suggesting a very floppy HCX bending potential characteristic of a quasilinear molecule.

The bending vibrational energy levels of the ground electronic state of HCCN have been calculated for a range of possible bending potentials by Malmquist *et al* [1] who carried out an *ab initio* study of the triplet ground electronic state of HCCN. As with all other *ab initio* calculations of the structure of ground state HCCN, they found the equilibrium geometry of the molecule is bent. Because all previous spectroscopic investigations of HCCN found the molecule to be linear, Malmquist *et al* provided the bending energy levels for a parametrically variable potential function capable of taking the bent *ab initio* potential all the way to linearity. The bending potential resulting from their parameterization that gives $\nu_5 \approx 190 \text{ cm}^{-1}$ is depicted above. This potential suggests that the HCC bond angle flops about linearity.

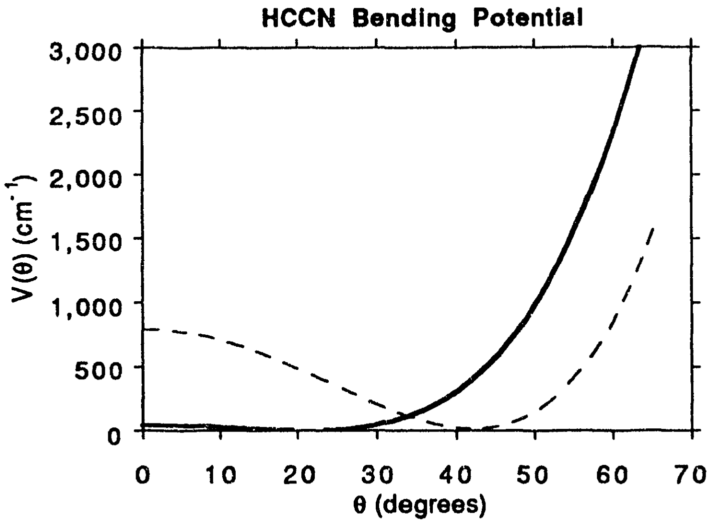

Figure 1. Potential function for the HCC angle agreeing with observed ν_5 energy. The molecule is linear when $\theta = 0$. The dashed curve is the *ab initio* (CCI) curve of Malmquist *et al.*

MEASUREMENT OF THE RATE CONSTANT FOR THE REACTION BETWEEN CCH AND H_2 AT ELEVATED TEMPERATURES

High temperature rate measurements on the reaction between C_2H and molecular hydrogen:

$$C_2H + H_2 \rightarrow H + C_2H_2 \qquad (2)$$

are crucial to a critical evaluation of the mechanism of acetylene pyrolysis,[2,3] which, of course, is an essential part of any more general hydrocarbon combustion mechanism. Since C_2H formation in such systems occurs primarily via the reverse of reaction (2), and since no experimental measurements of reaction (-2) exist, it is usual, when modelling either acetylene pyrolysis or combustion, to estimate the rate of reaction (-2) from the equilibrium constant, K_2, and the rate constant, k_2, for the forward reaction. Only one direct experimental investigation of the reaction between C_2H and H_2 at temperatures in excess of 300 K has been published.[4] This study suffers from two limitations: (1) It covered only a limited temperature range (298-438 K), and (2) only the ratio of k_2 to the rate of reaction of C_2H with acetylene, was measured. The only information concerning the rate of reaction (2) at combustion temperatures, comes from a TST calculation by Harding et al,[5] which utilized ab initio methods (POL-CI) for determining the properties of the potential energy surface in the saddle point region.

In our work, the rate of the reaction between C_2H and H_2 has been measured over the temperature range 295-855 K. The C_2H radical was produced by excimer laser photolysis of C_2H_2 at 193 nm, and its transient absorption was monitored throughout the reaction by using a tunable infrared color-center laser. The temperature dependence of the rate constant exhibited a non-Arrhenius form that could be well represented by the expression: $k = (9.44 \pm 0.50) \times 10^{-14}\, T^{0.9} \exp(-1003 \pm 40/T)$ cm^{3}molecule^{-1}s^{-1}. Figure 2 shows a comparison of our data with previous work.

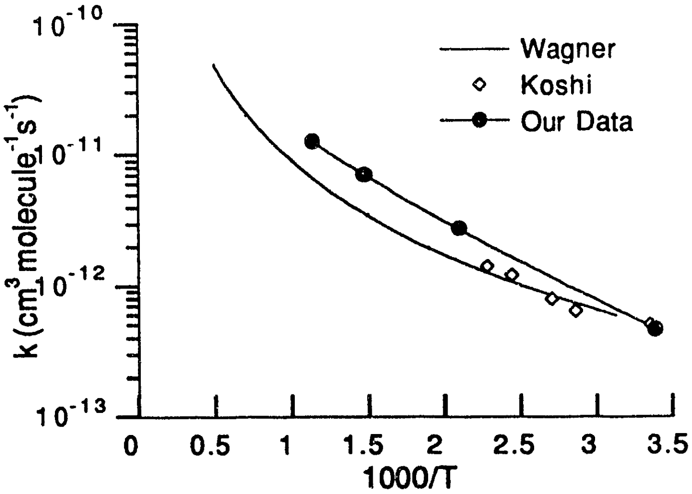

Fig. 2. The rate of the reaction, $C_2H + H_2$, as a function of temperature.

RECOMBINATION RATE OF PROPARGYL RADICAL

We reported last year an infrared kinetic spectroscopic investigation of the CH stretching fundamental of propargyl radical and described in our oral presentation preliminary measurements of the propargyl recombination rate at room temperature. Propargyl is produced by flash photolysis of propargyl bromide or chloride.

$$CH_2X\text{-}C\equiv CH + h\nu \rightarrow X + CH_2\text{-}C\equiv CH \qquad (3)$$

with X=Br or Cl. Another possible photolysis channel may be

$$CH_2X\text{-}C\equiv CH + h\nu \rightarrow HX + CH\text{-}C\equiv CH \qquad (4)$$

The time decay of the propargyl signal follows second order kinetics suggesting that propargyl is reacting with itself or another photolyis product. When X=Br, the Br atom can be observed with the same apparatus using the magnetic-dipole-allowed fine structure transition of the bromine atom at 3685 cm^{-1}. As the Br absorption cross section is known, the infrared absorption cross-section of propargyl can be determined by comparing its intensity to that of Br using the stoichiometry of reaction (3). The Br atom signal exhibits first order decay, which is faster than the propargyl decay under the same conditions. These observations show that propargyl does not react with the precursor C_3H_3Br nor with Br. When X=Cl, it is possible to observe transitions of the HCl vibrational fundamental. Indeed these appear promptly upon photolysis indicating that (4) is actually taking place. However, quantitative measurements establish that the ratio of moles HCl to moles C_3H_3 is 0.14 ± .02. Thus (4) is a minor channel when X=Cl, and the observed second order decay of propargyl must be caused by the reaction of propargyl with itself probably via recombination. These observations permit the determination of this recombination rate by measurement of the decay of the C_3H_3 concentration with time after photolysis of propargyl chloride. The resulting rate constant is 1.8(4) x 10^{-10} cm^3 $molecule^{-1}$ s^{-1}.

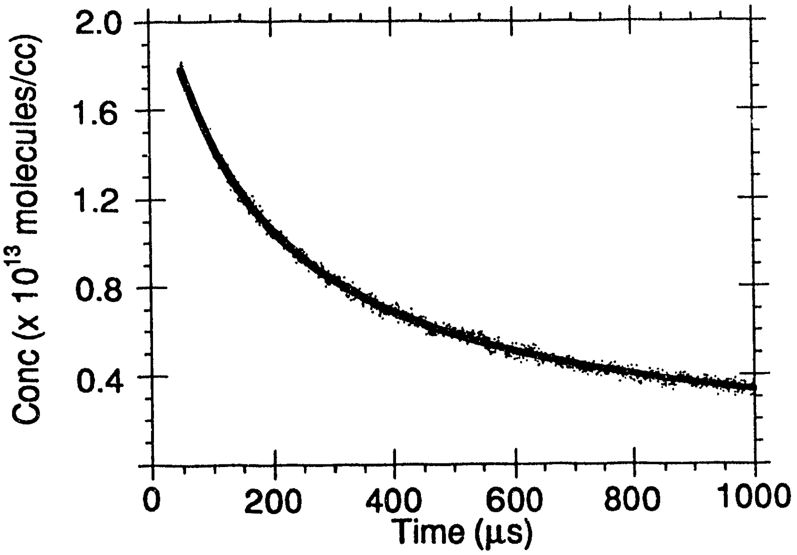

Fig. 3 Time decay of propargyl concentration fitted by second order kinetics expression.

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Publications

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2. "Rotationally Resolved Spectrum of the CH Stretch of the Propargyl Radical (H_2CCCH)," C. L. Morter, C. Domingo, S. K. Farhat, E. Cartwright, R. F. Curl, and G. P. Glass, Chem. Phys. Lett. **195**, 316-321 (1992).

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