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PROGRESS REPORT
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INFRARED ABSORPTION SPECTROSCOPY AND CHEMICAL KINETICS OF FREE
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PROPARGYL RADICAL

Effort during the last year has focussed primarily on propargyl (C_3H_3) radical. Propargyl has recently attracted interest because of its possible role in combustion and soot formation [1,2]. This radical is produced by reaction of methylene with acetylene [3-6]. At high temperatures it is not easily destroyed by dissociation [7] nor by reaction with oxygen [8]; thus, it has been observed in significant concentrations in numerous pyrolysis and oxidation processes [9-16]. In shock tube studies of propadiene and 1,2-butadiene, Kern and coworkers have proposed that propargyl recombination ($C_3H_3 + C_3H_3$) initiates benzene production [17,18]. This is of particular interest in understanding the mechanism for soot formation because there is evidence that benzene production is correlated with soot formation [19].

INFRARED SPECTRUM OF PROPARGYL RADICAL

Despite the importance of propargyl, little is known about its spectroscopy. Ramsay and Thistlethwaite observed an electronic absorption band of propargyl at $30,109\text{ cm}^{-1}$ [20], but predissociation in the excited state prevented them from resolving rotational structure. Infrared matrix isolation experiments [21,22] have been able to definitely assign only one vibrational transition of propargyl, the ν_1 stretch observed at 3309 cm^{-1} . ESR studies have determined that the propargyl structure has C_{2v} symmetry [23]. These investigations indicate that the most stable isomer of C_3H_3 is the propargyl radical structure ($H_2C-C\equiv CH$), in agreement with theoretical calculations [24,25]. However, none of these experiments have provided rotational data.

During the last year, we have obtained the high resolution spectrum of the ν_1 acetylenic CH stretch of propargyl radical ($HCCCH_2$) near 3322 cm^{-1} using infrared laser kinetic spectroscopy at Doppler limited resolution. Propargyl is prepared by flash photolysis of propargyl bromide (or propargyl chloride) at 193 nm (ArF excimer) and its transient infrared absorption probed by a cw color center laser. Fig. 1 shows a portion of the spectrum of propargyl near the ν_1 origin. This band consists as is expected of only a-type ($\Delta K=0$) transitions. In the region near the origin, the pattern is quite simple resembling the spectrum a diatomic molecule. This means that the A and D_K rotational constants in the upper state differ little from those of the ground state so that the various K subbands overlap almost exactly. Fig. 2 shows the K=1 asymmetry splittings for P(10). The K=1 lines are much weaker than the main feature. This can be explained on the basis that propargyl has C_{2v} symmetry with a

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2B_1 vibronic ground state: then the $K=1$ lines have a nuclear spin weight of 1 compared with spin weight 3 for even K . Ground and excited state rotational constants have been determined by fitting the $K=1$ lines having $N'' < 14$. As can be seen in Fig. 3, when $N \geq 14$ the spectrum no longer has a regular pattern probably because of perturbations of the excited state by nearby vibrational levels.

PROPARGYL RADICAL KINETICS

We are beginning to investigate the kinetics of propargyl radical. The decay of the radical after the flash, shown in Fig. 4, appears to be second order. The fine structure transition of the Br atom is accessible and when monitored under the same conditions as those of Fig. 4 appears to exhibit a simple first order decay suggesting that the Br atom is reacting with precursor propargyl bromide. In order to determine the propargyl recombination rate constant from the second order decay, the initial concentration of propargyl radical is required. This can be obtained from the intensity of the Br atom absorption as the infrared absorption cross-section of Br is known and the stoichiometry of the photolysis production mechanism makes the initial concentration of propargyl equal to that of Br.

However, the Br atom production branches between the ground $^2P_{3/2}$ and the upper $^2P_{1/2}$ state of the fine structure transition so that in order to obtain a reliable measure of the Br atom concentration, the population must be relaxed by the introduction of a suitable relaxant. About a torr of either CO_2 or H_2O is sufficient to relax Br in a microsecond. In the presence of the relaxant, we find that the initial Br signal increases by a factor of about 2.5 indicating that a significant fraction of the Br atoms are produced in the excited state. Work is currently in progress aimed at obtaining the rate of the propargyl recombination reaction by the Br atom calibration procedure.

KINETICS OF KETENYL RADICAL

Ketenyl radicals were produced by 193 nm excimer laser photolysis of ketene

and probed with a tunable diode laser operating at 2014 cm^{-1} . Under these conditions, any singlet methylene which may be formed via reaction 1b should react with the precursor, ketene, at a rate fast enough [26] to ensure its total removal from the photolysis cell within 1 μs .

In the presence of 2 to 8 Torr of O_2 , the ketenyl radical was observed to decay exponentially with time constants that ranged from 20 to 5 μs . A Stern-Volmer plot of the exponential decay rates is shown in Fig. 5. From this plot, the second order rate constant for the reaction of the ketenyl radical with O_2 at room temperature was determined as $6.5(6) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The rate constant thus obtained compares well with the value of $6.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ obtained by Peeters et al [27] but is more than an order of magnitude greater than the value of $3.7 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ obtained by Jones and Bayes [28].

Numerous experimental measurements indicate that, in lean hydrocarbon flames, the concentration of O_2 is at least 100 times greater than that of the various free radical species that are present [29]. In view of this, reaction with O_2 must be the major loss mechanism for HCCO in such flames.

The reaction of HCCO with molecular oxygen can occur in principal via any of the following channels:

An attempt was made to identify the most significant reaction pathway by determining the overall yield of CO. From such measurements the major reaction channel was tentatively identified as 3d, a channel which produces 2 molecules of CO for every molecule of HCCO consumed.

The observe decay of ketenyl was found to be largely unaltered by the addition of acetylene. By comparing the observed decay to that predicted in a number of computer simulations, an upper bound to the rate constant for the reaction between HCCO and acetylene of $1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ could be estimated.

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Publications

1. "Infrared Flash Kinetic Spectroscopy of the Ketenyl Radical," K. G. Unfried, G. P. Glass, and R. F. Curl, *Chem. Phys. Lett.* 177, 33-38.
2. "Acetylene Combustion Reactions: Rate Constant Measurements of HCCO with O₂ and C₂H₂," K. K. Murray, K. G. Unfried, G. P. Glass, and R. F. Curl, *Chem. Phys. Lett.* (accepted).
3. "Rotationally Resolved Spectrum of the CH Stretch of the Propargyl Radical (H₂CCCH)," C. L. Morter, C. Domingo, S. K. Farhat, E. Cartwright, R. F. Curl, and G. P. Glass, *Chem. Phys. Lett.* (submitted).

Theses

K. G. Unfried, Diode Laser Kinetic Spectroscopy (Ph.D.)

Figure Captions

Figure 1. An overview of the rotationally resolved ν_1 band of propargyl. Peaks marked with an asterisk (*) have been attributed to a hot band.

Figure 2. The $K=1$ asymmetry splitting for $P(10)$. The intensity ratio of the center peak to the $K=1$ satellite bands is in accord with that expected by propargyl spin statistics.

Figure 3. A portion of the P branch demonstrating that as N increases, perturbations are observed in the spectrum. Peaks marked with an asterisk (*) have been attributed to a hot band.

Figure 4. Main Figure: Second order kinetics plot of propargyl decay. Inset: Time trace of a propargyl absorption, resulting from the flash photolysis of C_3H_3Br at time $t=0$. Flow conditions were such that the gas, 50 mtorr C_3H_3Br in 18 torr He, was replenished every 18 seconds.

Figure 5. Stern-Volmer plot for the reaction of $HCCO$ and O_2 . Errors are estimated as $\pm 10\%$ of the measured pseudo first-order decay rate and are so indicated by the error bars on the plot. The second order rate constant of $6.5(6) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was determined from the slope of the least squares fit line.

IR ABSORPTION

IR ABSORPTION

Fig 2

IR ABSORPTION

Fig 3

1 / INTENSITY

Fig 4

FIG 5

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