PROGRESS REPORT
for
INFRARED ABSORPTION SPECTROSCOPY AND CHEMICAL-KINETICS OF FREE RADICALS

DE-FG05-85ER13439

DOE/ER/13439--5

DE90 009469

MARCH 1990

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PRESSURE EFFECTS IN REACTIONS OF C_2H WITH CARBON MONOXIDE AND ETHANE; C_2H RATE CONSTANTS

The time decay of an infrared transition originating from the ground state of C_2H has been followed by diode laser kinetic spectroscopy using excimer laser flash photolysis of trifluoropropyne to produce C_2H. Somewhat surprisingly, it was observed that C_2H reacts with CO. As no potential decomposition products of the hypothetical adduct HC_3O more stable than C_2H and CO appear to exist, it seemed likely that the reaction produces HC_3O stabilized by collision with a third body. Therefore, the dependence of the reaction rate upon buffer He gas pressure was studied. The pressure dependence, shown in Fig. 1, exhibits the expected proportionality of rate to He pressure. A third order rate constant of $2.4(6) \times 10^{-30}$ cm^6 $molec^{-2}$ s^{-1} was obtained for the reaction of C_2H with CO.

The dependence upon buffer He gas pressure of the rate constants of several other C_2H reactions was explored. As expected since the reaction almost certainly proceeds by H atom abstraction, no dependence of rate upon buffer gas pressure was observed in the reaction with CH_4. However, very surprisingly as this reaction would be expected to proceed by H atom abstraction also, a mild dependence of the rate of reaction of C_2H with C_2H_6 upon He pressure was observed and is depicted in Fig. 2. At a total pressure of 24 Torr, the apparent second order rate constant is $3.6(2) \times 10^{-11}$

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cm^3 $molec^{-1}$ s^{-1} for this reaction. It is difficult to visualize addition mechanisms for this reaction. Further studies aimed at determining the initial products of this reaction will be undertaken. Two other C_2H reactions with O_2 and CF_3CCH, in which addition is probably the first step, exhibit no dependence of rate upon He pressure. For these reactions the adduct is probably stabilized by collision at even the lowest pressure studied ($\approx$ 10 Torr).

Second order rate constants of $3{:}0(2)\times10^{-12}$, $1.3(3)\times10^{-10}$, $2.3(3)\times10^{-13}$ cm^3 $molec^{-1}$ s^{-1} were obtained for the reactions of C_2H with CH_4, C_2H_4, and D_2 respectively. The D_2 rate, when combined with our previous measurement of the rate of the H_2 reaction, gives an isotope ration H/D of 1.9, which is not far from the value of $\sqrt{2}$ expected for a loose transition state.

NO HNO PRODUCED IN THE THERMAL DeNOx PROCESS

In the accepted mechanism for the thermal deNOx process, the radical chain is maintained by branching into

$$NH_2 + NO \rightarrow N_2 + H_2O \qquad (1a)$$

$$\rightarrow HN_2 + OH \qquad (1b)$$

The species, HN_2, has been the subject of several *ab initio* calculations all of which predicted that it decomposes spontaneously on a sub-nanosecond timescale.

$$HN_2 \rightarrow H + N_2 \qquad (2)$$

Most observations on the reaction between NH_2 and NO find a channel producing OH, but several investigations have specifically sought H atoms without success suggesting the *ab initio* calculations may have underestimated the stability of HN_2 and that it may live long enough to react with NO, transferring its H atom and thereby avoiding the production of H atoms.

$$HN_2 + NO \rightarrow N_2 + HNO \qquad (3)$$

We have therefore searched for HNO in this system using diode laser kinetic spectroscopy producing NH_2 by 193 nm flash photolysis of NH_3 in the presence of NO and monitoring a known rotational component of the NH stretching vibration of HNO. No HNO signal is observed although we can easily observe HNO produced by reaction of HCO with NO in the same apparatus. We are currently quantifying these observations to establish an upper limit for the branching of NH_2 to HNO in the reaction system (1b) + (3).

PRODUCT BRANCHING RATIOS FOR NH_2 + NO BETWEEN 300 K AND 1200 K

The reaction between NH_2 and NO lies at the heart of the "Thermal DeNOx" process. Unfortunately, four recent measurements showing that the room temperature reaction yields predominantly N_2 and H_2O are inconsistent with the need of studies modelling the thermal deNOx process for a chain branching mechanism.

We reported last year that we had almost completed a study of the branching ratio between H_2O and OH for this reaction at four temperatures: 25, 400, 700, and 925 ^{0}C. The branching ratio was determined by comparison of the observed intensities of the OH and H_2O transient absorptions with the transient loss of absorption of NH_3 upon photolysis. This not only gives the fraction of NH_2 converted to OH or to water, but also shows how well these two product channels account for the reaction products. To do this, an infrared absorption cross-section for OH is required. We measured this relative to H_2O by relating OH to H_2O produced from the OH by two chemical kinetic schemes: the reaction at room temperature of OH produced by photolysis of HNO_3 with ethane and the reaction at 400 ^{0}C of OH (produced by reaction of $O(^1D)$ with H_2) with H_2. We submitted a paper on this OH cross-section to JQSRT which the editor indicated would be accepted, but shortly thereafter we learned of an OH cross-section measurement by Nesbitt that is about 40% higher than our value. After careful consideration, we concluded Nesbitt's results to be more reliable and withdrew our paper. The Nesbitt cross-section has the effect of making OH an even smaller channel. Thus our measurements on the deNOx reaction clearly make the accepted reaction scheme impossible because they indicate that the OH channel is far too small to support the process. Before publishing such a radical conclusion, we are rechecking our work.

Figure Legends

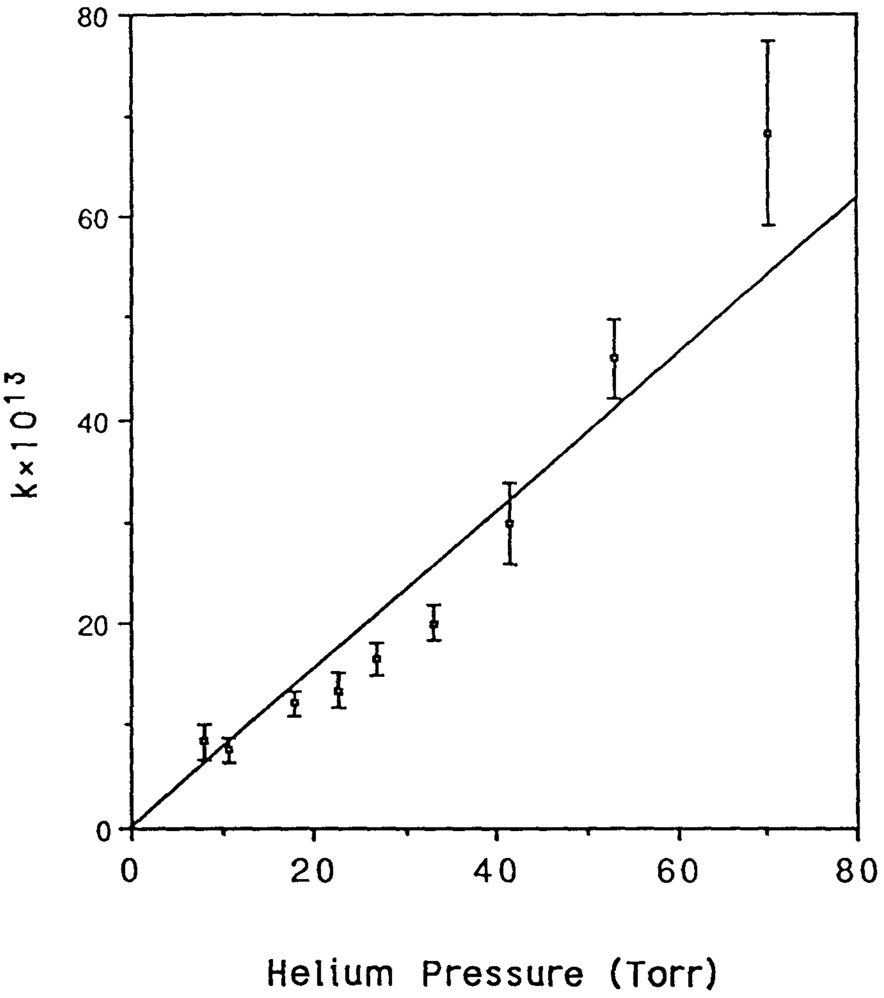
Figure 1. The second order rate constant of C_2H+CO plotted as a function of buffer helium pressure. Trifluoropropyne pressure ≈ 35-90 mTorr, SF_6 pressure ≈ 90-240 mTorr, CO pressure ≈ 600-1200 mTorr. The error bars are four estimated standard deviations of the second order rate constant in total length.

Figure 2. The second order rate constant of C_2H+C_2H_6 versus helium pressure. Trifluoropropyne pressure ≈ 35-90 mTorr, SF_6 pressure ≈ 80-270 mTorr, C_2H_6 pressure ≈ 35-60 mTorr. The error bars are four estimated standard deviations of the second order rate constant in total length.

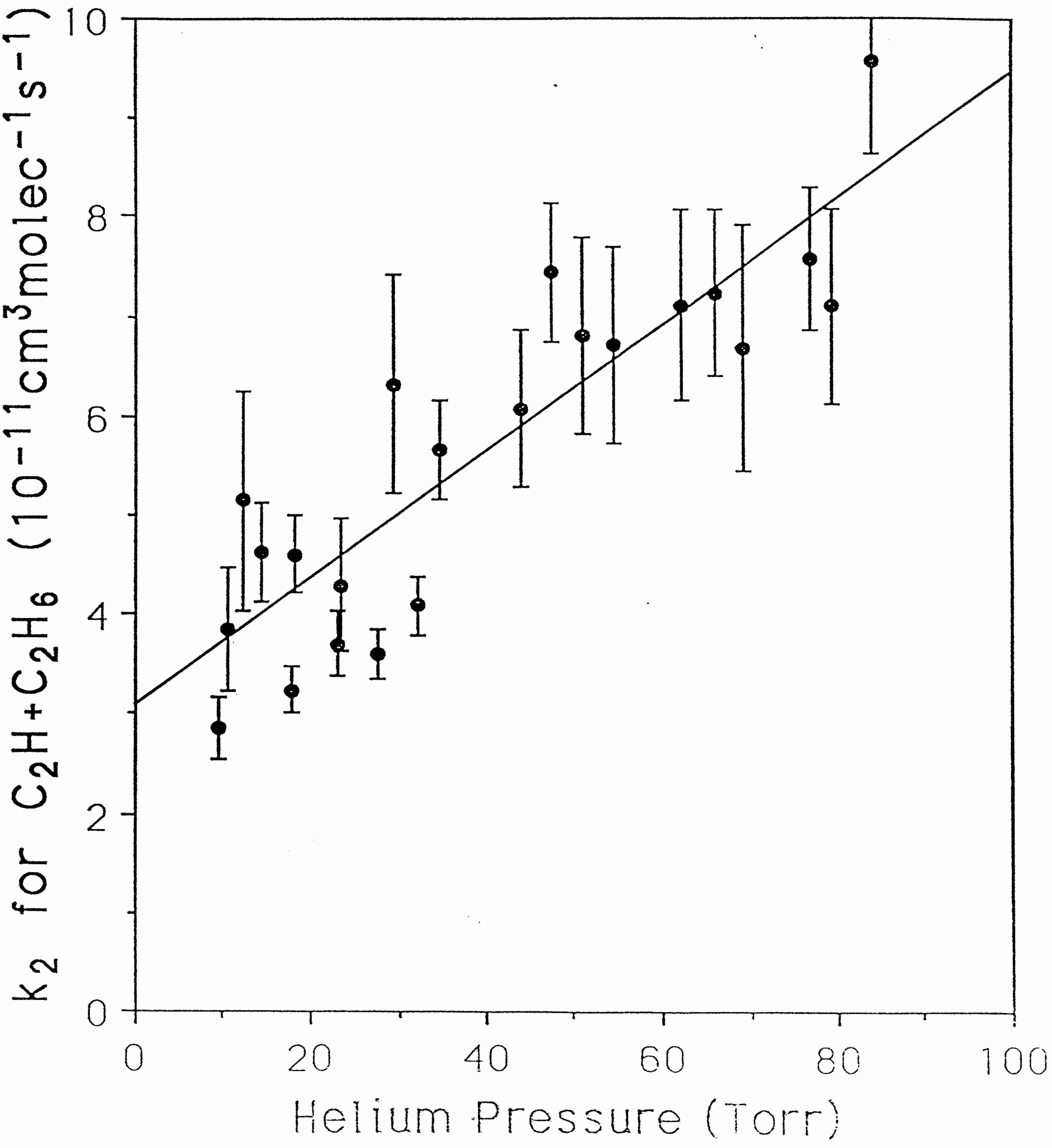
Publications

1. "Reaction Mechanism of $C_2H + O_2$", D. R. Lander, K. G. Unfried, J. W. Stephens, G. P. Glass and R. F. Curl, *J. Phys. Chem.* **93**, 4109-4116 (1989).

2. "Rate Constant Measurements of C_2H with CH_4, C_2H_6, C_2H_4, D_2, and CO", D. R. Lander, K. G. Unfried, G. P. Glass, and R. F. Curl, *J. Phys. Chem.* (accepted).



80
60
40
20
0
k×10^13
0
20
40
60
80
Helium Pressure (Torr)


k_2 for $C_2H+C_2H_6$ $(10^{-11}cm^3molec^{-1}s^{-1})$
0
2
4
6
8
10
0
20
40
60
80
100
Helium Pressure (Torr)