PROGRESS REPORT
for
INFRARED ABSORPTION SPECTROSCOPY AND CHEMICAL KINETICS OF FREE RADICALS
DE-FG05-85ER13439

MARCH 1989

Robert F. Curl and Graham P. Glass
Principal Investigators

DOE/ER/13439--4

DE89 010089

REACTION MECHANISM OF C_2H WITH O_2

In a previous study of the reaction between C_2H and O_2, we measured an overall reaction rate constant that was much faster than those obtained by other workers. We rationalized this result, in part, by suggesting that a long-lived intermediate is formed in the reaction, and that C_2H removal is much faster than final product formation. With the additional sensitivity provided by the modifications to the apparatus, we have been able to test this hypothesis by monitoring infrared transition frequencies of C_2H, HCO, OH, HO_2, CO, and CO_2 as a function of reaction time.

C_2H was generated in the presence of a large excess of O_2 by flash photolysis of acetylene and trifluoropropyne at 193nm. Only two products were actually observed, CO and CO_2, with the amount of CO produced being approximately 5 times larger than the amount of CO_2 produced. All of the CO_2 was produced at long reaction times, clearly showing it to be a secondary product. HCO, OH, and HO_2 were not detected, although our sensitivity for detecting the first two of these species should have been good. Evidence for significant production of atomic hydrogen was obtained by adding NO_2 to the system, and detecting the OH produced by the rapid reaction, $H + NO_2 \rightarrow OH + NO$.

Vibrationally excited states of both CO and CO_2 are produced by the reaction. For CO vibrational quantum numbers could be assigned; excited state transitions of CO up to v = 7←6 were observed. When using acetylene as a precursor, vibrational relaxation of CO is extremely slow, and it was possible to uncouple chemical formation of the excited states from collisional de-excitation. Under these conditions, there appear to be two distinct processes leading to CO formation, a fast process forming vibrationally excited CO at a rate that approximately matched the rate of C_2H decay, and a much slower process producing predominantly low vibrational states of CO. The fast, direct, process was the only one observed for v = 5←4 and higher, and the slow process was the only one discernible for the v = 1←0 transition. Figure 1, which was recorded under conditions such that vibrational relaxation was negligible, clearly shows the different rates of formation of various states of CO.

The fast, direct, process forming vibrationally excited CO was identified as $C_2H + 02 \rightarrow H + 2CO$. Other thermodynamically possible, direct, channels producing HCO + CO, OH + C_2O, and CH + CO_2 could be excluded because of the absence of HCO, OH, CD (using C_2D_2) and "prompt" CO_2 respectively.

The rate of the slow process producing lower vibrational states of CO exhibited saturation behavior with increasing O_2 pressure. In order to reproduce the observed kinetics, a model involving at least two intermediates between C_2H and CO was postulated. The probable identity of the first intermediate is the peroxy radical HC_2O_2, formed by addition, although no direct proof of this was obtained.

Finally, it should be mentioned that the large discrepancy between the rate constant measured in this laboratory and that measured by Laufer and Lechleider has been completely resolved. When CO (v=1←0) was monitored under conditions similar to those used by Laufer and Lechleider, a signal risetime almost identical to that reported by them was obtained. It is now clear that this risetime results from a combination of vibrational relaxation by trifluoropropyne of excited CO produced by the direct mechanism and ground state CO produced by the indirect mechanism.

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 have 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. Figure 2 is a bar graph summarizing our preliminary results.

Figure Legends

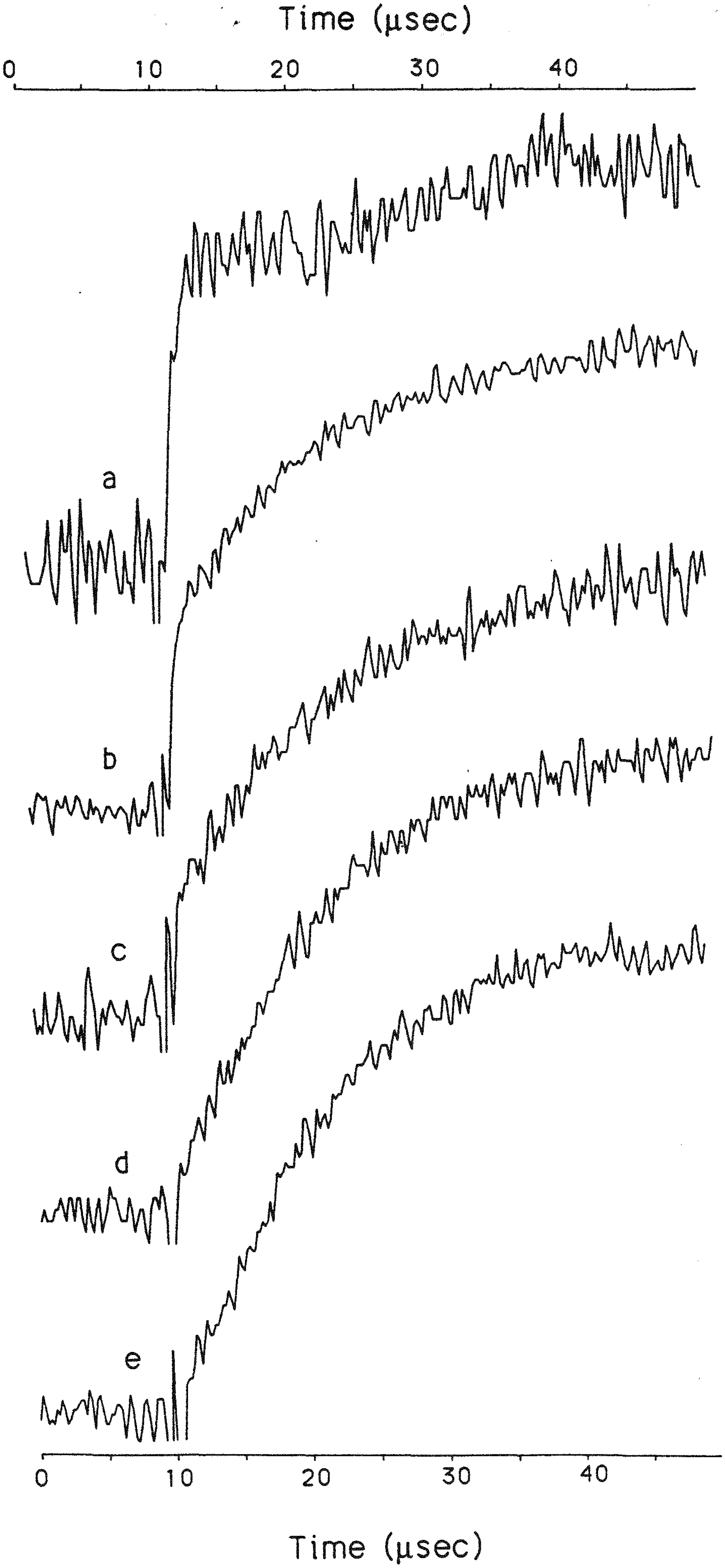
Figure 1. Comparison of the CO signals arising from different vibrational transitions on a short time scale. (a) CO($v=5\leftarrow4$) R(14) absorption signal; (b) CO($v=4\leftarrow3$) R(6) absorption signal; (c) CO($v=3\leftarrow2$) R(2) absorption signal; (d) CO($v=2\leftarrow1$) P(4) absorption signal; (e) CO($v=1\leftarrow0$) P(12) absorption signal.

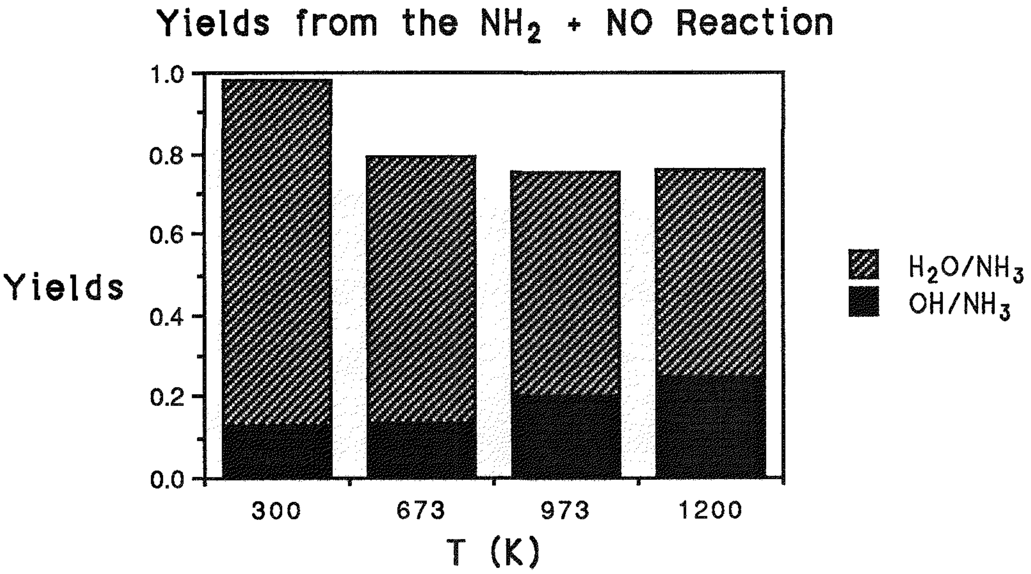
Figure 2. Yields of OH and H_2O for the reaction NH_2 + NO studied at 4 different temperatures. NH_3 pressure = 15 mTorr, NO pressure = 400 mTorr, SF_6 pressure = 400 mTorr, He pressure = 18 Torr.

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.* (in press).

2. "Absorption Cross-section for the OH Fundamental", J. W. Stephens, G. P. Glass and R. F. Curl, *J. Quant. Spect. and Rad. Transfer* (submitted).


Time (μsec)
0
10
20
30
40
a
b
c
d
e
0
10
20
30
40
Time (μsec)


Yields from the NH_2 + NO Reaction
1.0
0.8
0.6
0.4
0.2
0.0
Yields
300
673
973
1200
T (K)
▨ H_2O/NH_3
■ OH/NH_3