

## Preliminary Note

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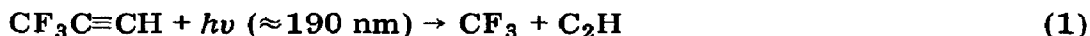
### Evidence for HF elimination via a five-centered complex in the photodissociation of 3,3,3-trifluoropropyne near 200 nm

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It was suggested by Howarth and Sherwood [1] that the primary process in the photolysis of 3,3,3-trifluoropropyne in the 190 nm region is the dissociation of the compound to give ethynyl and trifluoromethyl radicals:



The only volatile product they observed was the trimer of trifluoropropyne, 1,3,5-tris(trifluoromethyl)benzene, which they attributed to a radical-catalyzed polymerization reaction. They also noted the formation of a non-volatile solid polymer. The production of the  $\text{CF}_3$  and  $\text{C}_2\text{H}$  radicals was confirmed by the formation of  $\text{CF}_3\text{H}$  and  $\text{C}_2\text{H}_2$  upon the addition of propane.

In our study of the flash photolysis of  $\text{CF}_3\text{C}_2\text{H}$  in an optical cavity we observed HF stimulated emission, indicating that vibrationally excited HF was produced. The mechanism for the HF production is not immediately obvious, because ground state  $\text{CF}_3\text{C}_2\text{H}$  is probably a symmetric top molecule with the H atom at the opposite end of the  $\text{C}_3$  axis from the  $\text{CF}_3$  group. In this work we investigated the mechanism of the HF formation.

#### 1. Experimental

This study was carried out in a UV-VUV flash laser system which is very similar to that described previously [2]. Briefly, a laser tube of length 1 m and i.d. 1.2 cm, which was alternately Suprasil, quartz or Vycor, fitted with a  $\text{BaF}_2$  Brewster window and connected to a glass vacuum line, was positioned in an optical cavity formed by an internal gold-coated mirror and a grating (blazed at  $2.7 \mu\text{m}$ , with an efficiency of approximately 90% between 2.6 and  $3.2 \mu\text{m}$ ). The gap between the grating and the Brewster window was continually flushed with dry  $\text{N}_2$  to avoid atmospheric water absorption of emitted radiation.

A 3.0 cm i.d.  $\times$  80 cm flashlamp was coaxially mounted to the laser tube by two 2.5 - 1.3 cm Cajons with appropriate O-rings. The energy for the flash was produced by an 18 kV d.c. power supply and stored in a  $14 \mu\text{F}$  capacitor. A 30 kV pulse generator triggered the spark gap. The resulting flash output had a  $5 \mu\text{s}$  rise time and a  $7 \mu\text{s}$  half-width.

HF laser emissions were analyzed by a 0.5 m Minuteman 305M13 monochromator fitted with a kinematically mounted grating (150 lines  $\text{mm}^{-1}$ , blazed at  $6 \mu\text{m}$ ) and were observed with a liquid  $\text{N}_2$  cooled Ge–Au detector in conjunction with a Tektronix 7633 storage oscilloscope.

All gases used in this work were obtained from the Matheson Gas Products Company, except the  $\text{CF}_3\text{C}_2\text{H}$ , which was obtained from PCR, Inc. Condensable chemicals were subjected to trap-to-trap distillation using appropriate slush baths. Non-condensables were used without further purification.

## 2. Results and discussion

HF laser emission was observed when mixtures of  $\text{CF}_3\text{C}_2\text{H}$  and Ar or  $\text{SF}_6$  were flash photolyzed in Suprasil (above 165 nm) and quartz (above 190 nm) laser tubes. No emission was detected when the mixtures were photolyzed in Vycor (above 220 nm). HF emission from both the  $2 \rightarrow 1$  and  $1 \rightarrow 0$  transitions was observed in the Suprasil and quartz tubes.

The grating selection method [3, 4] was used to achieve single line oscillation, and the appearance times of all lines were measured. The relative vibrational population distributions were determined with the aid of plots of the relative gain *versus* population ratio based on the well-known gain equation [5, 6]. A relative population distribution of  $N_0:N_1:N_2 = 1.0:0.63:0.30$  was found for all mixtures. This result was independent of  $\text{CF}_3\text{C}_2\text{H}$  concentration, diluent choice and laser tube. This distribution corresponds to a vibrational temperature of approximately  $10^4$  K, with the excited HF carrying more than  $7 \text{ kcal mol}^{-1}$  of vibrational energy.

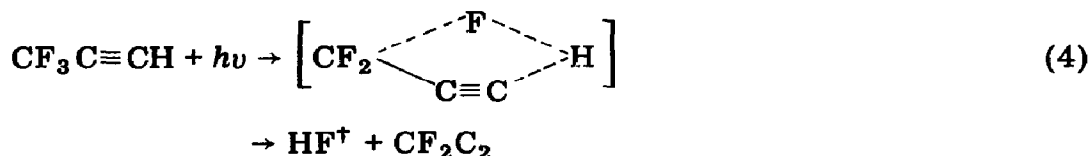
The most obvious mechanism for the HF formation corresponds to the production of an F atom, followed by hydrogen abstraction, according to the following mechanism:



However, this mechanism can be ruled out for two reasons. First, the energy released in reaction (3),  $\Delta H_3 = -11 \pm 2 \text{ kcal mol}^{-1}$  (assuming  $D_0(\text{CF}_3\text{C}_2 - \text{H}) = D_0(\text{C}_2\text{H} - \text{H}) = 124 \pm 1 \text{ kcal mol}^{-1}$  [7]), is barely enough to excite HF to  $v = 1$ . Experimentally, HF emission from  $v \leq 2$  was observed, as mentioned earlier. Second, a direct test for the mechanism was carried out by adding  $\text{D}_2$  to mixtures of  $\text{CF}_3\text{C}_2\text{H}$  in Ar. Essentially no DF emission was observed, indicating that F atoms were not produced to any appreciable extent in the initial photodissociation reaction.

To rule out any possible laser pumping mechanisms involving  $\text{CF}_3$ ,  $\text{CF}_3\text{I}$  (a source of  $\text{CF}_3$  as well as F) was added to a reaction mixture of  $\text{CF}_3\text{C}_2\text{H}$  in Ar. Rather than an enhancement in laser power, a slight reduction in total power was observed, indicating that the only effect the additional  $\text{CF}_3$  (or F and  $\text{CF}_3\text{I}$ ) had on the reaction was to quench the lasing species.

A third and probably the most likely mechanism of HF production is the direct photoelimination of HF from a five-membered ring complex:



This mechanism seems plausible because the first excited state of acetylene,  $\tilde{\text{A}}^1\text{A}_u$  (via  $\tilde{\text{X}}^1\Sigma_g^+ \rightarrow \tilde{\text{A}}^1\text{A}_u$  at 237 - 210 nm) is bent, with the HCC angle =  $120^\circ$  [8]. If an excited state of  $\text{CF}_3\text{C}\equiv\text{CH}$  is bent with a cis-configuration, the hydrogen would be brought very near to a fluorine, permitting formation of a five-membered ring complex with subsequent elimination of excited HF from the ring.

To confirm this mechanism, attempts will be made to intercept chemically the product  $\text{CF}_2\text{C}_2$  radical by employing appropriate scavengers. In the pure  $\text{CF}_3\text{C}_2\text{H}$  system, as employed by Howarth and Sherwood [1],  $\text{CF}_2\text{C}_2$  may rapidly disappear by addition to the parent molecule, resulting in polymerization. HF cannot be readily detected by a gas chromatographic method which may explain why reaction (4) was not observed in a conventional photolytic study, even though it occurs to such an extent as to generate stimulated emission.

To our knowledge, reaction (4) is the only laser pumping reaction that takes place via a five-membered ring elimination complex. Most elimination laser systems known to date are either three-centered [2, 9] or four-centered [6, 10 - 12] elimination reactions.

Further work will be carried out to confirm the mechanism of HF production. We also plan to carry out multiphoton dissociation of  $\text{CF}_3\text{C}_2\text{H}$  in the  $1000\text{ cm}^{-1}$  region (corresponding to several combination bands in the absorption spectrum), using an intense pulsed  $\text{CO}_2$  laser, to study the dynamics of the dissociation in the ground electronic state.

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