

UV Photodissociation Dynamics of Furan

J. J. Wang, Naoki Hemmi and Arthur G. Suits

Lawrence Berkeley National Laboratory, University of California, Berkeley, CA 94720, USA

We have studied the photodissociation of furan, C_4H_4O , at 193nm (Fig. 1) on endstation 1 of the Chemical Dynamics Beamline using tunable undulator radiation as a probe of the neutral photofragments. Furan is one of the simplest oxygen-containing aromatic molecules, and its dissociation exhibits both molecular and radical decay channels that can provide insight into the dynamics of ring-opening and H-migration pathways in these systems. In these studies, a continuous supersonic molecular beam of furan in helium is crossed by the output of a pulsed excimer laser at 193nm. Neutral fragments travel 15cm into the triply differentially pumped detector region where they are ionized by broadband (2.2% bandwidth) undulator radiation, with the resulting ions mass selected using a quadrupole mass filter, then counted as a function of time and scattering angle.¹

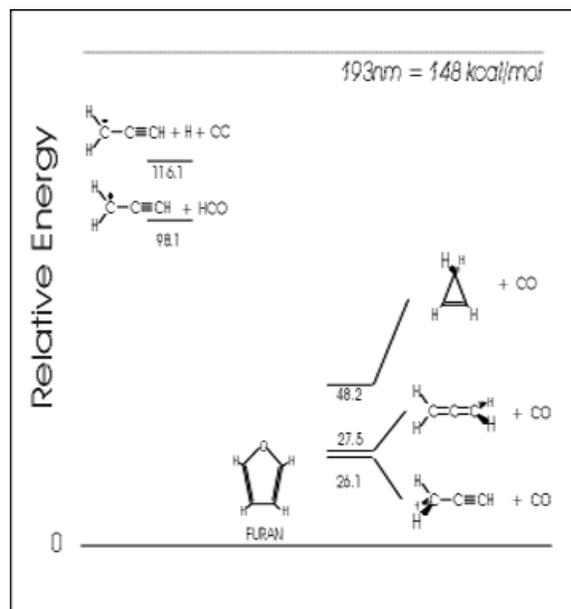


Figure 1. Energetics for possible pathways in decomposition of furan following excitation at 193nm.

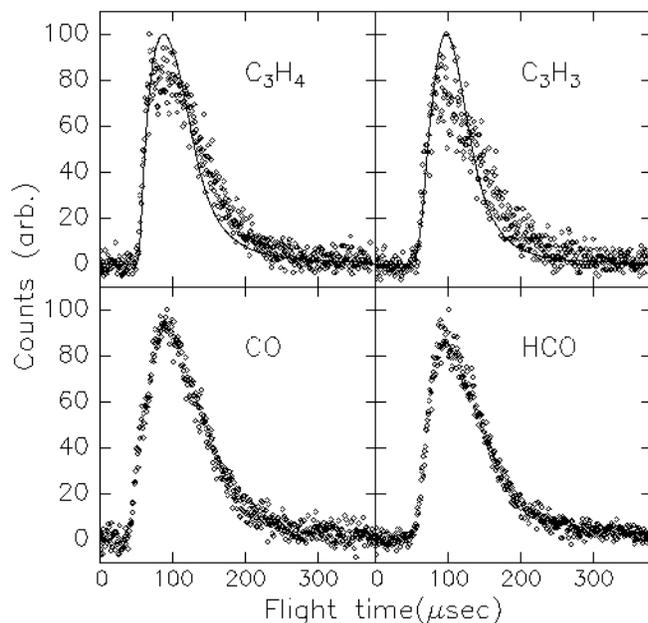


Figure 2. Time-of-flight spectra for four observed fragments of furan photodissociation at 193nm recorded at a laboratory scattering angle of 10 degrees. Fragment identity and probe photoionization energy are indicated in each spectrum.

We observe only two channels in this dissociation process: a molecular channel yielding $C_3H_4 + CO$, and a radical channel giving $C_3H_3 + HCO$. These latter species are both key radicals in hydrocarbon combustion chemistry. Fig. 2 shows time-of-flight spectra for these four fragments at a laboratory angle of 10 degrees, along with simulations that are used to generate the translational energy distributions. Both channels show relatively little of the available energy appearing in translation, but the distributions peak away from zero energy, indicating a likely exit barrier. It is interesting that we observe no H or H₂ elimination in this system, in striking contrast to the dissociation of pyrrole, C_4H_4NH , the analogous N-containing system.² It is clear from the fact that we observe only these two dissociation channels that opening of the ring is the

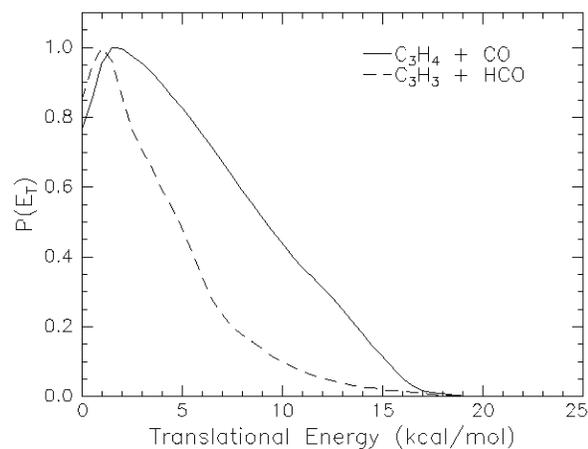


Figure 3. Total center-of-mass translational energy distributions for the two primary channels indicated.

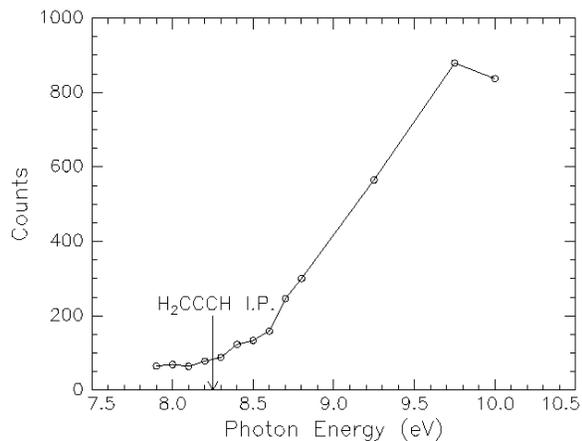


Figure 4. Photoionization efficiency spectrum of C_3H_3 photofragment.

initial step. The radical channel can then result immediately from C-C bond fission, although H migration is then necessary in the C_3H_3 fragment in order to yield the lowest energy H_2CCCH isomer. Using the tunable undulator radiation, we can probe the photoionization efficiency of this radical product; this is shown in Fig. 4 along with the threshold indicated for the C_3H_3 isomers.

For the molecular channel, three product isomers are possible for C_3H_4 : these are propyne, H_3CCH , allene, H_2CCH_2 and cyclopropene, *c*- C_3H_4 . On the basis of the photoionization dependence of that molecule we can likely eliminate the formation of cyclopropene as an important component. The differences in the ionization potentials of allene and propyne are too small, however, to allow us to distinguish them on this basis. In addition to the primary contributions to the CO and HCO products, we observe some CO arising from secondary decomposition of the HCO. With further analysis, we hope to use this process to quantify the branching between these two channels.

REFERENCES

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2. D. A. Blank, S. North and Y. T. Lee, *Chem. Phys.*, (1996).

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Principal investigator: Arthur G. Suits, MS 10-110, Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley CA 94720. Email agsuits@lbl.gov.