EVIDENCE FOR DISSOCIATION FROM THE S_0 GROUND STATE OF ACETALDEHYDE TO THE RADICAL PRODUCTS CH_3 and HCO

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Recent experiments and theory have implicated a "roaming" mechanism as being important in the photodissociation of CH_3CHO into the molecular products CH_4 + CO.[a,b] As much as 80% of the flux for this chemical channel was attributed to roaming; the conventional transition state mechanism is a minor contribution. Quasi-classical trajectory calculations reveal that many of these roaming trajectories can be described as a methyl group roaming around the HCO core, before intramolecularly abstracting the formyl H atom. A crucial element to this mechanism is that the simple, barrierless, C-C bond cleavage to radical products must be open at the wavelengths used in previous experiments. While there is no doubt that the radical channel is open in an energetic sense, HCO and CH_3 have never been observed from the ground state (S_0) surface. In this seminar, we will summarize the evidence for roaming in CH_3CHO and then present new experimental evidence that HCO and CH_3 are indeed formed on the ground state.

Pump/probe experiments were performed on acetaldehyde seeded in a supersonic expansion of helium. HCO products were probed via laser-induced fluorescence ($\tilde{B} \leftarrow \tilde{X}$) at a range of pump wavelengths (308 - 330 nm). When the pump energy was above the (T_1) barrier for dissociation ($\lambda \sim$320 nm),[c] the HCO product state distribution is characteristic of a reaction proceeding over a barrier. When the dissociation energy is lower than the triplet barrier, HCO was still observed, which must then arise from reaction on the S_0 surface. In addition, the HCO internal energy distribution was different when dissociating above and below the triplet barrier, thereby confirming the presence of two different mechanistic pathways. The existence of the CH_3 + HCO channel from the CH_3CHO ground state supports the previous assignment of "CH_3 roaming" in CH_3CHO photodissociation to CH_4 + CO.

[a] P. L. Houston and S. H. Kable, *PNAS*, **103**, 16079 (2006).
[b] B. R. Heazlewood *et al, submitted* (2006).
[c] S.-H. Lee and I.-C. Chen, *Chem. Phys.*, **220**, 175 (1997).