

## EVIDENCE FOR DISSOCIATION FROM THE $S_0$ GROUND STATE OF ACETALDEHYDE TO THE RADICAL PRODUCTS $\text{CH}_3$ and $\text{HCO}$

ALAN T. MACCARONE, B.R. HEAZLEWOOD, S.J. ROWLING, S.H. KABLE, *School of Chemistry, University of Sydney, Sydney NSW 2006, Australia.*

Recent experiments and theory have implicated a "roaming" mechanism as being important in the photodissociation of  $\text{CH}_3\text{CHO}$  into the molecular products  $\text{CH}_4 + \text{CO}$ .<sup>a,b</sup> 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  $\text{HCO}$  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,  $\text{HCO}$  and  $\text{CH}_3$  have never been observed from the ground state ( $S_0$ ) surface. In this seminar, we will summarize the evidence for roaming in  $\text{CH}_3\text{CHO}$  and then present new experimental evidence that  $\text{HCO}$  and  $\text{CH}_3$  are indeed formed on the ground state.

Pump/probe experiments were performed on acetaldehyde seeded in a supersonic expansion of helium.  $\text{HCO}$  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),<sup>c</sup> the  $\text{HCO}$  product state distribution is characteristic of a reaction proceeding over a barrier. When the dissociation energy is lower than the triplet barrier,  $\text{HCO}$  was still observed, which must then arise from reaction on the  $S_0$  surface. In addition, the  $\text{HCO}$  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  $\text{CH}_3 + \text{HCO}$  channel from the  $\text{CH}_3\text{CHO}$  ground state supports the previous assignment of "CH<sub>3</sub> roaming" in  $\text{CH}_3\text{CHO}$  photodissociation to  $\text{CH}_4 + \text{CO}$ .

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<sup>a</sup>P. L. Houston and S. H. Kable, *PNAS*, **103**, 16079 (2006).

<sup>b</sup>B. R. Heazlewood *et al*, *submitted* (2006).

<sup>c</sup>S.-H. Lee and I.-C. Chen, *Chem. Phys.*, **220**, 175 (1997).