HYDROGEN EXCHANGE BEFORE DISSOCIATION IN THE PHOTOLYSIS OF ACETALDEHYDE: A NON-TRANSITION STATE MECHANISM.

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Non-transition state (TS) reaction mechanisms continue to attract a great deal of attention, experimentally and theoretically, because they challenge the paradigms of kinetic theories. The "roaming" mechanism was first described 5 years ago in the photolysis of H_2CO.[a] It was originally described as a non-TS mechanism, although recent work has characterized a "roaming" TS, which is very flat, and without a well-defined structure. In addition, roaming reactions may re-cross this TS many times in an excursion from reactant to product and so conventional TS theories are still inadequate for predicting the rate of such reactions. Photolysis of the more complex acetaldehyde (CH_3CHO) has proven to be a benchmark molecule for studies of roaming because the higher molecular complexity, and the near energetic equivalence of the TS to CH_4 + CO and the C-C bond cleavage to CH_3 + HCO produces a much higher flux of roaming reactions.[b]

In this seminar, we shall present experimental results on the photolysis of isotopically-labeled acetaldehyde, CD_3CHO, and, hopefully, CH_3CDO. Photolysis of CD_3CHO is shown to produce almost 10% of the radical flux as DCO products. We have performed *ab initio* calculations of the critical points on the global C2, D3, H, O potential energy surface at energies below the experimental photolysis energy, revealing several pathways to DCO products. From these theoretical energies, vibrational frequencies and rotational constants we have calculated RRKM rates for each forward and reverse reaction on this surface. A master equation analysis of the product rates predicts that the yield of DCO, via these conventional TS pathways, should only be $< 0.1\%$, which is about two orders of magnitude less than observed experimentally. We have not included the known roaming pathway to CH_4 + CO, but that would only reduce the DCO product. The mechanism for the observed DCO production is at the present time unknown, but we hypothesise that another roaming-type mechanism might efficiently exchange the H and D atoms, producing a transient CD_2HCDO intermediate which then dissociates in a conventional mechanism to produce CD_2H + DCO.

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[a] D. Townsend, *et al.*, *Science* **306**, 1159, (2004)

[b] B. R. Heazlewood, *et al.*, *Proc. Nat. Acad. Sci., USA* **105**, 12719, (2008)