

## LOW TEMPERATURE REACTION KINETICS OF CN( $v=1$ ) WITH BUTADIENE ISOMERS.

SHAMEEMAH THAWOOS, *Department of Chemistry, University of Missouri, Columbia, MO, USA*; GREGORY HALL, *Division of Chemistry, Department of Energy and Photon Sciences, Brookhaven National Laboratory, Upton, NY, USA*; CARLO CAVALLOTTI, *Department of Chemistry, Materials, and Chemical Engineering "G. Natta", Politecnico di Milano, Milano 20133, Italy*; ARTHUR SUITS, *Department of Chemistry, University of Missouri, Columbia, MO, USA*.

Formation pathways and mechanisms of unsaturated nitrogen-containing compounds at very low temperatures are of great interest in the field of astrochemistry. The reaction of butadiene isomers with CN is one such reaction class that can be a key elementary step in the formation of large nitrogen rich molecules of potential biological importance in astrochemical environments. We present a joint experimental and theoretical investigation of reaction kinetics of vibrationally excited CN with 1,3 and 1,2-butadiene isomers at 70 K. The experimental method involves a newly built apparatus that couples a pulsed uniform supersonic flow with a continuous wave cavity ringdown spectrometer (UF-CRDS). The well-matched hydrodynamic time of the uniform flow with the long ringdown time decay allows the measurement of the complete kinetics over observation times up to 200  $\mu\text{s}$  on each ringdown decay, an approach termed SKaR (Simultaneous kinetics and ringdown). The vibrationally excited CN is produced by photolyzing BrCN with a 248 nm excimer laser. The adjustable butadiene density greatly exceeds that of the photolytic CN radicals, ensuring pseudo first order conditions for the loss of CN. The time-dependent density of CN( $v=1$ ,  $j=5.5$ ) is probed by tuning the DFB diode laser at 7070.24  $\text{cm}^{-1}$ , the  $R_1(5.5)$ , line of the (0-1) band of  $A^2\Pi-X^2\Sigma^+$  electronic transition. The measured bimolecular rates are  $(3.96 \pm 0.28) \times 10^{-10}$  and  $(3.06 \pm 0.35) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for 1,3 and 1,2-butadiene, respectively. The experimental rates were modeled by VRC-TST (Variable Reaction Coordinate Transition State Theory) calculations on a high-level multireference potential energy surface. For the 1,2-butadiene case the entrance channel branching was combined with earlier predictions of branching following the decays of the initial adducts to predict the overall branching.