PHOTODISSOCIATION DYNAMICS OF VINYL CYANIDE STUDIED BY CHIRPED-PULSE MILLIMETER-WAVE SPECTROSCOPY OF HCN AND HNC PRODUCTS

KIRILL PROZUMENT, RACHEL G. SHAVER, JOSHUA H. BARABAN, G. BARRATT PARK, *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139*; ARTHUR G. SUITS, *Department of Chemistry, Wayne State University, Detroit, MI 48202*; JOHN S. MUENTER, *Department of Chemistry, University of Rochester, Rochester, NY 14627*; ROBERT W. FIELD, *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139*.

Vinyl cyanide 193 nm photodissociation has been studied using Chirped-Pulse Millimeter-Wave (CPmmW) spectroscopy. $J = 0 - 1$ transitions of more than 30 vibrationally excited states of the HCN and HNC products have been recorded and assigned within the 7 GHz wide chirp range. Bending excitations of HCN up to $v_2 = 14$, leading toward the HCN $\leftrightarrow$ HNC isomerization transition state, are detected and interpreted in terms of their electric quadrupole, $(eQq)_{\mathrm{N}}$, and rotational, B_v, constants. The photolysis reaction transition states were probed using both normal vinyl cyanide, CH_2=CHCN, and its singly-deuterated isotopologue, CH_2=CDCN. The observed difference in the vibrational population distribution (VPD) obtained from the integrated intensities of the HCN and DCN products from the CH_2=CHCN vs. CH_2=CDCN photolysis reactions, suggests the relative unimportance of the three-center elimination mechanism for HCN production. On the other hand, the similarity in the observed VPD and overall intensities of HCN from CH_2=CHCN and CH_2=CDCN photolysis suggests four-center elimination as the major mechanism leading to the HCN product. Additional $J - (J + 1)$ transitions would be required to characterize both the vibrational and the rotational state distributions of the products, which would permit more complete characterization of the transition state(s). The authors thank the Department of Energy, and KP thanks the ACS Petroleum Research Fund for their support of this work.