CN is one of the most abundant and widespread radicals in the interstellar medium. The fast reactions between CN and neutral hydrogen radicals generate various nitriles \( ^2 \), including HC3N and H2CCCN, which are alleged to be probe molecules for HCN in interstellar environments. Similarly, H2CCCN has also been detected in numerous objects, such as the dark cloud TMC-1, massive star-forming regions Sgr B2 and Orion KL, the circumstellar envelope of the C-rich star IRC-10216, and Titan's atmosphere. Because of the wide distribution of these species, it is interesting to explore if the reactivity of CN with HCN and H2CCCN can produce more complex nitriles. Kinetics studies confirmed that the rate constant for the CN(\( ^2 \)) + HCN reaction increases rapidly as the temperature decreases from 300 K to 22 K \( ^\circ \), while few studies have focused on the CN(\( ^2 \)) + H2CCCN reaction. Furthermore, there are no experimental data on the reaction products and their branching ratios. Given these open questions, it is essential to gain further insights into these elementary reactions, both experimentally and theoretically.

Introduction

The potential energy surface of each system was investigated by locating the lowest stationary points at the B3LYP level of theory \( ^3 \) in conjunction with the correlation consistent valence polarized split aug-cc-pVTZ basis set. At the same level of theory we have computed the harmonic vibrational frequencies in order to check the nature of the stationary points, i.e., minimum if all the frequencies are real, saddle point if there is one, and only one, imaginary frequency. The assignment of the saddle points was performed using intrinsic reaction coordinate (IRC) calculations \( ^4,5 \). The energy of selected stationary points was computed also at the higher level of calculation CCSD(T) using the same basis set aug-cc-pVTZ \( ^1,6,7 \). The CCSD(T) energies were corrected to 0 K by adding the zero point energy correction computed using the scaled harmonic vibrational frequencies evaluated at B3LYP/aug-cc-pVTZ level. All calculations were done using Gaussian \( ^8 \) and the optimized geometries were visualized using ACD/ChemDraw Ultra \( ^9 \).

\[ \text{Theory} \]

\[ \text{Experiment} \]

We have investigated the CN(\( ^2 \)) + HCN and CN(\( ^2 \)) + CH2CN reactions by the CMB method in its "universal" arrangement with mass spectrometric (MS) detection and time-of-flight (TOF) analysis by employing hard electron ionization (70 eV). From product angular and velocity distribution measurements in the laboratory frame, at different mass-to-charge (m/z) ratios, we have identified the primary product channels, derived the product angular and translational energy distributions (TOD) and PIQD, respectively, in the centre-of-mass frame, and determined the product branching ratios (BRs).

\[ \text{Main Results:} \]

At the collision energy of 44.69 kJ/mol, the reaction of CN(\( ^2 \)) with HCN proceeds through the barrierless addition of CN by C-aside to the unsaturated carbon-carbon triple bond of HCN leading to a bound intermediate, followed by the fission of a C-H bond to produce 2-Butynedinitrile (NCCHCN) + H with an exit barrier. NCCCHCN radical is internally very hot. From the CM (70%) distribution, the only one exothermic channel can take place through indirect mechanism. That means the stable intermediate INT1 is able to exist for several rotational periods before dissociating to form the final product.

\[ \text{Astrophysical Implications} \]

- The CN(\( ^2 \)) + HCN reaction is an effective process in the atmosphere of Titan and the interstellar medium (ISM), where it leads to the NCCCHCN product. The first experiment to measure the primary product conducted by us verified the accuracy of the developed models in which this reaction is included.
- The CN(\( ^2 \)) + CH2CN reaction could play a role in the formation of more complex nitriles (i.e., NCCCHCN, Z-NCCCHCN, and HC3CCCN) in the atmosphere of Titan and the interstellar medium (ISM). This reaction could fast below room temperatures and thus should be included in the gas-phase model.

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\[ \text{References:} \]


