MILLIMETER WAVE SPECTROSCOPY OF THE VINYL RADICAL (HDC=CH) GENERATED BY UV LASER PHOTOLYSIS IN A PULSED SUPERSONIC JET EXPANSION

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The vinyl radical has tunneling motion of acetylenic (CH) proton. The proton tunneling transitions of the vinyl radical, both for the normal (H_2CCH) and deuterated species (H_2CCD), were observed by millimeter wave spectroscopy and the proton tunneling splittings of H_2CCH and H_2CCD in the ground state have been determined 16271.8429(59) MHz and 1164.861(20) MHz, respectively. The HDCCH is a mono-deuteride of the methylenic (CH_2) proton of the vinyl radical, and may have two local potential minima; cis- and $trans$-forms, where cis-HDCCH has an unpaired electron on the same side of deuterium with respect to the C=C double bond, while $trans$-HDCCH on the opposite side. If the energy difference Δ_{ct} between the ground state of $trans$-HDCCH and that of cis-HDCCH is small enough, the proton tunneling transition will be observed. On the other hand, if Δ_{ct} is large ($\Delta_{ct} \geq 1$ cm^{-1}), the b-type rotational transitions of $\Delta K_a = \pm 1$ will be observed in cis- and $trans$-tautomers instead of the tunneling transition between the cis- and $trans$-forms.

In the present study, the rotational spectra of the cis-HDCCH have been observed by millimeter wave spectroscopy combined with a pulsed supersonic jet technique. The HDCCH radical was generated by 193 nm excimer laser photolysis of mono-deuteride vinyl chloride(HDCCHCl). The a-type rotational transitions of the cis-HDCCH,$N_{K_a K_c}$=$2_{02}-1_{01}$, $3_{03}-2_{02}$, were observed in the frequency region of 109$-$164 GHz. The observed rotational lines were split into fine and hyperfine components due to spin-rotation interaction and spin-nuclear spin interaction. The molecular constants such as rotational constants, spin-rotation interaction constant, and hyperfine interaction constants were determined by least squares fitting. These molecular constants are consistent with the results of the millimeter wave spectroscopy of H_2CCH and H_2CCD in gas phase, and result of ESR study in Ar matrix [a]. The rotational spectra of the $trans$-HDCCH have not been observed in supersonic jet (15 K). This fact suggests that the ground state of $trans$-HDCCH is much higher than that of cis-HDCCH. The zero point energy difference Δ_{ct} between cis- and $trans$-forms, calculated to be 38 cm^{-1} from the CCSD(T)/cc-pVTZ calculation, supports the present result by millimeter wave spectroscopy.

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[a] P. H. Kasai,*J. Am. Chem. Soc.* **94**, 5950 (1972)