CONFORMATIONAL ISOMERIZATION KINETICS OF VINYL ISOCYANATE MEASURED BY DYNAMIC ROTATIONAL SPECTROSCOPY

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Vinyl isocyanate (CH_2=CH–N=C=O) can exist in two stable conformations, having a *cis* or *trans* arrangement about the C-N single bond. Electronic structure calculations indicate that the *trans* conformer is about 250 cm^{-1} lower in energy. There is a low barrier to isomerization of the *trans* conformer calculated to be about 580 cm^{-1}. These energetics are supported by the pure rotational spectrum of vinyl isocyanate in a molecular beam, where transitions of the *trans* conformer are about 300 times stronger than those of the *cis* conformer due to conformational relaxation in the free-jet expansion. The dominance of the *trans* conformer guarantees that vibrational excited states prepared by pulsed infrared laser excitation are effectively conformer-selective. Dynamic rotational spectra of laser-prepared excited states in the 3000 cm^{-1} region of the spectrum show evidence of conformational isomerization through coalescence of the overall line shape. Strong mode-specific reaction yields are observed from different vibrational bands where, in some frequency regions, there is no evidence of conformational isomerization despite the molecule having a total vibrational energy greatly exceeding the barrier to reaction. The nuclear quadrupole hyperfine structure of the dynamic rotational spectra shows that isomerization, when it occurs, conserves the K_a angular momentum projection quantum number.