

INFRARED SPECTRA OF C₂H₄Br AND C₂H₄I IN SOLID *para*-HYDROGEN: BRIDGED OR OPEN STRUCTURE?

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The electrophilic addition of halogens to alkenes is important in organic synthesis. The structure of the reaction intermediate, haloalkyl radical, plays an important role in the stereo specificity of the addition reaction. The simplest intermediate, haloethyl radical C₂H₄X, has two possible geometries: an open (classical) structure and a bridged structure. However, which structure is more stable is controversial because several calculations yield varied results. Experiments using time-resolved X-ray diffraction^a and UV absorption^b indicated that C₂H₄I has a bridged structure, but our results of Cl + C₂H₄ in solid *para*-hydrogen (*p*-H₂) indicated that C₂H₄Cl has an open structure.^c Even though experiments in noble-gas matrices suggest that C₂H₄Br is open,^d whereas C₂H₄I is bridged,^e the spectral evidence remains uncertain.

We took advantage of the diminished cage effect of *p*-H₂ to investigate the infrared (IR) spectra of C₂H₄Br and C₂H₄I by irradiating *p*-H₂ matrices containing C₂H₄ and Br₂ or I₂ with light at varied wavelengths. New spectral lines were grouped according to their behavior upon subsequent annealing and secondary photolysis. The assignments were derived on comparison with scaled vibrational wavenumbers and IR intensities calculated with the B3LYP/aug-cc-pVTZ-pp method. Our preliminary results indicate that lines at 676.9, 776.7, 1068.1, 1148.0, and 3126.8 cm⁻¹ are assigned to the 2-bromoethyl radical (C₂H₄Br) in an open form, whereas those at 933.7, 1139.0, 1436.8, and 1609.0 cm⁻¹ to the iodoethyl radical (C₂H₄I) in the bridged form. A small amount of C₂H₄Br₂ and C₂H₄I₂ was also observed; their stereochemistry will also be discussed.

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