INFRARED SPECTRA OF THE 1,1-DIMETHYLALLYL AND 1,2-DIMETHYLALLYL RADICALS ISOLATED IN SOLID $PARA$-HYDROGEN

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The reaction of hydrogen atoms (H) with isoprene (C_5H_8) in solid $para$-hydrogen (p-H_2) matrices at 3.2 K has been studied using infrared spectroscopy. The production of H atoms for reaction with C_5H_8 was essentially a three step process. First, mixtures of C_5H_8 and Cl_2 were co-deposited in p-H_2 at 3.2 K for several hours, then the matrix was irradiated with ultraviolet light at 365 nm to produce Cl atoms from the Cl_2, and finally the matrix was irradiated with infrared light to induce the reaction of the Cl atoms with p-H_2 to produce HCl and H atoms. Upon infrared irradiation, a series of new lines appeared in the infrared spectrum, with the strongest lines appearing at 776.0 and 766.7 cm^{-1}. To determine the grouping of lines to distinct chemical species, secondary photolysis was performed using a 365-nm light-emitting diode and a low-pressure mercury lamp in combination with filters. Based on the secondary photolysis, it was determined that the majority of the new lines belong to two distinct chemical species, designated as set X (3030.6, 1573.2, 1452.0, 1435.6, 1123.2, 1051.4, 982.7, 922.5, 792.5, 776.0, 699.2, 524.7, 469.0 cm^{-1}) and set Y (3110.1, 2972.0, 1564.4, 1471.1, 1430.2, 1379.7, 1376.2, 1335.4, 1233.0, 1205.4, 1050.1, 766.7, 570.0 cm^{-1}). The most likely reactions to occur under the low temperature conditions in solid p-H_2 are the addition of the H atom to the four alkene carbon atoms to produce the corresponding hydrogen atom addition radicals (HC_5H_8). Quantum-chemical calculations were performed at the B3PW91/6-311++G(2d,2p) level for the four possible HC_5H_8 radicals in order to determine the relative energetics and the predicted vibrational spectra for each radical. The addition of H to each of the four carbons is exothermic, with relative energies of 0.0, 93.3, 77.0, and 8.4 kJ/mol for the addition to carbons 1 – 4, respectively. When the lines in set X and Y are compared to the scaled harmonic and anharmonic vibrational spectra, the best agreement for set X is with the radical produced by the addition to carbon 4 (1,2-dimethylallyl radical) and the best agreement for set Y is with the radical produced by addition to carbon 1 (1,1-dimethylallyl radical).