INFRARED SPECTRA OF THE 1-CHLOROMETHYL-1-METHYLALLYL AND 1-CHLOROMETHYL-2-METHYLALLYL RADICALS ISOLATED IN SOLID $PARA$-HYDROGEN

JAY C. AMICANGELO, *School of Science (Chemistry), Penn State Erie, Erie, PA, USA*; YUAN-PERN LEE, *Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan, Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan*.

The reaction of chlorine atoms (Cl) with isoprene (C_5H_8) in solid $para$-hydrogen (p-H_2) matrices at 3.2 K has been studied using infrared spectroscopy. Mixtures of C_5H_8 and Cl_2 were co-deposited in p-H_2 at 3.2 K, followed by irradiation at 365 nm to cause the photodissociation of Cl_2 and the subsequent reaction of Cl atoms with C_5H_8. Upon 365 nm photolysis, a series of new lines appeared in the infrared spectrum, with the strongest appearing at 807.8 and 796.7 cm^{-1}. To determine the grouping of lines to distinct chemical species, secondary photolysis was performed using a low-pressure Hg lamp in combination with various filters. Based on the secondary photolysis behavior, it was determined that the majority of the new lines belong to two distinct chemical species, designated as set A (3047.2, 1482.2, 1459.5, 1396.6, 1349.6, 1268.2, 1237.9, 1170.3, 1108.8, 807.8, 754.1, 605.6, 526.9, 472.7 cm^{-1}) and set B (3112.7, 1487.6, 1382.6, 1257.7, 1229.1, 1034.8, 975.8, 942.4, 796.7, 667.9, 569.7 cm^{-1}). The most likely reactions to occur between Cl and C_5H_8 under the low temperature conditions in solid p-H_2 are the addition of the Cl atom to the four distinct alkene carbon atoms to produce the corresponding chlorine atom addition radicals (ClC_5H_8). Quantum-chemical calculations were performed at the B3PW91/6-311++G(2d,2p) level of theory for the four possible ClC_5H_8 radicals in order to determine the relative energetics and the predicted harmonic vibrational spectra for each radical. The calculations predict that the addition of Cl to each of the four carbons is exothermic, with relative energies of 0.0, 74.5, 67.4, and 7.9 kJ/mol for the addition to carbons 1 – 4, respectively. When the lines of set A and B are compared to the scaled harmonic vibrational spectra for all four of the possible Cl addition radicals, it is found that the best agreement for set A is with the radical produced by the addition to carbon 4 (1-chloromethyl-2-methylallyl radical) and the best agreement for set B is with the radical produced by addition to carbon 1 (1-chloromethyl-1-methylallyl radical). Therefore, the lines of set A and B are assigned to these radicals, respectively.