INFRARED SPECTROSCOPY OF 1-CHOLOROMETHYLALLYL AND 1-METHYLALLYL RADICALS PRODUCED IN A SOLID PARA-HYDROGEN MATRIX.

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The reaction of chlorine atoms with trans-1,3-butadiene in solid para-hydrogen (p-H_2) matrix has been studied using Fourier transform infrared spectroscopy. When a mixture of Cl_2, trans-1,3-butadiene and p-H_2 was deposited onto a cold target at 3 K and irradiated by UV light at 365 nm, new intense lines at 809.0, 962.1, 1240.6 cm^{-1} and several weaker ones appeared. The carrier of this spectrum was assigned to the 1-chloromethylallyl radical, •(CH_2CHCH)CH_2Cl, based on the anharmonic vibrational frequencies calculated with the DFT method, indicating that the addition of the Cl atom to trans-1,3-butadiene occurs primarily at the terminal carbon atom. This is in sharp contrast to the reaction of chlorine atoms with propene in a solid p-H_2 matrix[a] in which the addition of Cl to the central carbon atom to produce selectively the 2-chloropropyl is favored due to the steric effects. The energy diagram calculated with B3PW91 method supports this selective reaction process because 1) the channel from trans-1,3-butadiene to 1-chloro-methylallyl is almost barrierless (0.4 kcal/mol), and 2) isomereization from 1-chloromethylally to the 2-chloro-3-buten-1-yl radical, $CH_2CHCHClCH_2$•, by migration of Cl atom from the terminal to the central C atom, hardly occur in the p-H_2 matrix because of the isomerization barrier height (18.8 kcal/mol). We also observed a second set of lines with intense ones at 781.6, 957.93, 1433.6 cm^{-1} and several weaker ones when the UV-irradiated Cl_2/trans-1,3-butadiene/p-H_2 matrix was further irradiated with infrared light from a globar source. These lines are assigned to the 1-methylallyl radical, •(CH_2CHCH)CH_3, produced from reaction of 1,3-butadiene with an H atom that was produced from the reaction of Cl atoms with IR-irradiated p-H_2, Cl + H_2^* → H + HCl. The energy diagram calculated at the G3//B3LYP level[b] similarly supports the reaction process to form selectively 1-methylallyl in the p-H_2 matrix.

[a] J. C. Amicangelo and Y. P. Lee, *J. Phys. Chem. Lett.* **1**, 1956 (2010).
[b] J. L. Millerngelo, *J. Phys. Chem. A* **108**, 2268 (2004).