DIMINISHED CAGE EFFECT IN p-H_2: IR IDENTIFICATION OF INTERMEDIATES IN ADDITION REACTIONS OF CL ATOM WITH UNSATURATED HYDROCARBONS

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We report infrared absorption spectra of several free radicals produced upon reaction of Cl atoms with unsaturated hydrocarbons isolated in solid p-H_2. Cl atoms were produced by in situ photodissociation of Cl_2 isolated in solid p-H_2 at 365 nm. In experiments with the $Cl_2/C_6H_6/p$-H_2 matrices, intense absorption features at 617.0, 719.8, 956.0, and 1430.5 cm^{-1} and weaker ones at 577.1, 833.6, 876.8, 833.6, 983.0, 993.5, 1008.0, 1026.4, 1112.5, 1118.5, 1179.0, 1406.5, 1509.4, 2967.2, 3054.3, 3063.4, 3070.9, and 3083.9 cm^{-1} appeared upon irradiation of the matrix at 365 nm and increased in intensity upon subsequent annealing of the matrix at 4.8 K for a few minutes. By comparison of vibrational wavenumbers and deuterium isotopic shifts predicted with the B3PW91 and MPW1PW91/aug-cc-pVTZ methods, these features are readily assigned to the σ-complex of ClC_6H_6 (chlorocyclohexadienyl radical), rather than the previously proposed π-complex. In experiments with the $Cl_2/C_2H_2/p$-H_2 matrices, the 1-chloroethyl radicals ($CHClCH_3$) and chloroethene (C_2H_3Cl) are identified as the main products of the Cl + C_2H_2 reaction in solid p-H_2. The assignments of IR absorption lines at 738.2, 1027.6, 1283.4, 1377.1, 1426.6, 1442.6, and 2861.2 cm^{-1} to 1-chloroethyl radicals are based on comparison of the observed vibrational wavenumbers and ^{13}C- and D-isotopic shifts with those predicted with the B3LYP and MP2/aug-cc-pVDZ methods. These results indicate that the primary products of the addition reaction Cl + C_2H_2, the 2-chlorovinyl radicals, are unstable; they react readily with p-H_2 to form $CHClCH_3$ and C_2H_3Cl. If time permits, other examples such as Cl + 1, 3-butadien and H + C_6H_6 or C_6H_5Cl will be discussed. These results serve as excellent examples to demonstrate that the diminished cage effect of solid p-H_2 makes production of free radicals via bimolecular reactions feasible.