

DIMINISHED CAGE EFFECT IN *p*-H₂: 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*-H₂. Cl atoms were produced by in situ photodissociation of Cl₂ isolated in solid *p*-H₂ at 365 nm. In experiments with the Cl₂/C₆H₆/*p*-H₂ 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 ClC₆H₆ (chlorocyclohexadienyl radical), rather than the previously proposed π -complex. In experiments with the Cl₂/C₂H₂/*p*-H₂ matrices, the 1-chloroethyl radicals (CHClCH₃) and chloroethene (C₂H₃Cl) are identified as the main products of the Cl + C₂H₂ reaction in solid *p*-H₂. 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 ¹³C- 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 + C₂H₂, the 2-chlorovinyl radicals, are unstable; they react readily with *p*-H₂ to form CHClCH₃ and C₂H₃Cl. If time permits, other examples such as Cl + 1, 3-butadien and H + C₆H₆ or C₆H₅Cl will be discussed. These results serve as excellent examples to demonstrate that the diminished cage effect of solid *p*-H₂ makes production of free radicals via bimolecular reactions feasible.