INFRARED SPECTRA OF THE 2-CHLOROPROPYL RADICAL IN SOLID PARA-HYDROGEN

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The reaction of chlorine atoms with propylene and one of its deuterium isotopomers in solid *para*-hydrogen (p-H_2) matrices at 3.2 K has been studied using infrared spectroscopy. Irradiation at 365 nm of a co-deposited mixture of Cl_2, C_3H_6, and p-H_2 at 3.2 K produces a series of new lines in the infrared spectrum. Several of the new lines are readily assigned to the gauche and trans conformers of 1,2-dichloropropane ($CH_3CHClCH_2Cl$) resulting from the addition of two Cl atoms to C_3H_6. Weak lines observed at 802 and 975 cm^{-1} and at 813 and 981 cm^{-1} that become more prominent upon secondary irradiation at 254 and 214 nm are assigned to the allyl radical (C_3H_5) and an HCl-allyl radical complex (HCl-C_3H_5), respectively[a]. Of the remaining lines, a strong line at 650 cm^{-1} and weaker lines at 532, 1008, 1133, 1150, 1215 and 1382 cm^{-1} are concluded to be due to a single carrier based on their behavior upon subsequent annealing to 4.5 K and irradiation at 254 and 214 nm. When the positions and intensities of these lines are compared to the MP2/aug-cc-pVDZ predicted vibrational spectra of the possible species that could result from the addition and abstraction reactions of one Cl atom with C_3H_6[a], the best agreement is found with the 2-chloropropyl radical ($CH_3CHClCH_2\cdot$). Isotopic experiments were performed with 3,3,3-$C_3H_3D_3$ and the corresponding infrared peaks due to the deuterium isotopomer of this radical ($CD_3CHClCH_2\cdot$) have also been observed. A final set of experiments were performed following irradiation of the Cl_2/C_3H_6/p-H_2 mixture at 365 nm, in which the matrix was irradiated with filtered infrared light from a globar source, which has been shown to induce a reaction between isolated Cl atoms and matrix H_2 to produce HCl and H atoms[b]. In our experiments, the major products observed after infrared irradiation are HCl, 2-chloropropane ($CH_3CHClCH_3$) and the isopropyl radical ($CH_3CH{\cdot}CH_3$) and the possible mechanisms of formation of these species will be discussed.

[a] P. Brana and J. A. Sordo, J. Comput. Chem. 24, 2044 (2003)
[b] P. L. Raston and D. T. Anderson, Phys. Chem. Chem. Phys. 8, 3124 (2006)