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

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The reaction of chlorine atoms with ethylene and two of its deuterium isotopomers in solid para-hydrogen (\(p\)-H\(_2\)) matrices at 3 K has been studied using infrared spectroscopy. Irradiation at 365 nm of a co-deposited mixture of Cl\(_2\), C\(_2\)H\(_4\), and \(p\)-H\(_2\) at 3 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-dichloroethane (\(\text{CH}_2\text{CICH}_2\text{Cl}\)) resulting from the addition of two Cl atoms to C\(_2\)H\(_4\). Of the remaining lines, a strong line at 664 cm\(^{-1}\) and three weaker lines at 562, 1070, and 1228 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\(_2\)H\(_4\), the best agreement is found with the 2-chloroethyl radical (\(\cdot\text{CH}_2\text{CH}_2\text{Cl}\)). In order to confirm this assignment, isotopic experiments were performed with C\(_2\)D\(_4\) and t-C\(_2\)H\(_2\)D\(_2\) and the corresponding infrared bands due to the deuterium isotopomers of this radical (\(\cdot\text{CD}_2\text{CD}_2\text{Cl}\) and \(\cdot\text{CHDCHDCl}\)) have been observed. A final set of experiments were performed following irradiation of the Cl\(_2\)/C\(_2\)H\(_4\)/\(p\)-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 were HCl and ethyl chloride (\(\text{CH}_3\text{CH}_2\text{Cl}\)) and the possible mechanism of the formation of ethyl chloride will be discussed.