Determining the Products and Mechanism of the C₂Cl₃+O₂ Reaction by Time-Resolved FTIR Emission Spectroscopy

HONGMEI SU, TIANCHENG XIANG, SHAOLEI ZHAO, CONGYUN SHI — The reaction products and mechanism of the C₂Cl₃ radical with O₂ have been studied by time-resolved FTIR emission spectroscopy. The chlorinated vinyl radical, C₂Cl₃, was generated by 248 nm photolysis of a C₂Cl₄ precursor. Vibrationally excited CO, CO₂ and ClCO products were observed. The time evolution of the emission intensity shows that CO₂ and ClCO are primary reaction products. In contrast, CO emission does not decay until ms time scale indicating that CO products are due to secondary reactions, most likely, the further dissociation of ClCO. Two primary reaction channels are identified: C₂Cl₃ + O₂ → CO₂ + ClCl → ClCO + COCl₂ When reacting with O₂, the observed products and channels of the chlorinated vinyl radical, C₂Cl₃, turned out to be very similar to its counterpart, vinyl radical C₂H₃. Morokuma’s DFT study[1] of the reaction C₂H₃+O₂ shows that the main reaction path proceeds through a three-membered CCO ring adduct. The question is, does C₂Cl₃ go through the same reaction path as C₂H₃? Does the substitution of H atom by heavier Cl atom make any difference in regard to the reaction mechanism? Further investigation combining ab initio calculation is under way.


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