MICROWAVE IDENTIFICATION OF KEY INTERMEDIATES IN VENUS ATMOSPHERE: ClCO AND $\mathrm{ClC(O)OO}$

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The atmosphere of Venus is primarily composed of $\mathrm{CO_2}$ (96.5%), $\mathrm{N_2}$ ($\sim$3.5%), Ar (0.01%), and trace amounts of other chemical compounds. Although $\mathrm{CO_2}$ is supposed to be dissociated to CO and $\mathrm{O_2}$ by solar ultraviolet radiation, an enormous amount of $\mathrm{CO_2}$ still exists in Venus's atmosphere. In the $\mathrm{CO_2}$ cycle, the ClCO and $\mathrm{ClC(O)OO}$ are critical in the reactions, being the intermediates in the reactions.[a] The pure rotational transitions of ClCO and $\mathrm{ClC(O)OO}$ were measured using Fourier transform microwave spectroscopy in the region of 8 GHz to 40 GHz. In the case of ClCO, both the isotopologues $^{35}\mathrm{ClCO}$ and $^{37}\mathrm{ClCO}$ were observed, while only a-type transitions with K_a = 0 were observed due to the fairly large rotational constant A. When it comes to $\mathrm{ClC(O)OO}$, which was expected to be produced from the reaction of ClCO and $\mathrm{O_2}$, both cis-$\mathrm{ClC(O)OO}$ and trans-$\mathrm{ClC(O)OO}$ were observed. Fine and hyperfine components of both conformers were well-assigned, leading to the precisely determined fine and hyperfine constants. The trans-$\mathrm{ClC(O)OO}$ radical is a prolate asymmetric top molecule with rotational constants $A > B \approx C$, while the cis-$\mathrm{ClC(O)OO}$ is more like an oblate top molecule with rotational constants $A \approx B > C$. The unpaired electrons on both $\mathrm{ClC(O)OO}$ conformers are mainly on out-of-plane π orbitals of the terminal oxygens of the COO moiety. Moreover, due to the position of the unpaired electron, the hyperfine coupling constants of chlorine are very small.

[a] W. B. DeMore, Yuk L. Yung, Catalytic Processes in the Atmospheres of Earth and Venus. Science, 217, 1209-1213 (1982)