

Study of tropospheric CS₂ photooxidation chemistry

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Abstract

Carbon disulfide (CS₂) is an atmospheric trace gas whose main sources in the atmosphere are from oceans and soils (Khalil et al., 1984). Anthropogenic emissions have increased in recent years, producing a strong regional distribution. CS₂ is a reactive atmospheric sulfur gas, and as such it has a relatively short lifetime, ranging from a few days to half a month (Khan et al., 2017). Its oxidation end products in the atmosphere are carbonyl sulfide (COS) and sulfur dioxide (SO₂). Therefore, CS₂ indirectly contributes to the production of sulfate aerosols, which influence atmospheric radiative properties and stratospheric ozone depletion.

The OH-initiated oxidation of CS₂ in the presence of O₂ is considered to be the main CS₂ sink pathway. By forming an intermediate SCSOH at first, followed by a series of oxidation reactions with O₂ to produce COS and SO₂, this process removes 75~88% of atmospheric CS₂ (Khan et al., 2017). The current literature suggests that the conversion ratio of CS₂ to COS is 0.83 (Stickel et al., 1993), but this result may be underestimated because only reaction with OH radicals considered and CS₂ photochemistry is neglected.

The mechanism of CS₂ photooxidation was first proposed by Wine et al. (1981). According to the CS₂ UV-Vis absorption spectrum, there is a strong absorption band at 280~360 nm, which would first photo excite CS₂ from ground state to CS₂(³A₂) state (usually presented as CS₂^{*} state). Then the majority of CS₂^{*} particles will be de-excited into CS₂ ground state molecules after collision with air molecules (N₂, O₂ and H₂O). Because of the rapid photochemical reaction rate of CS₂, a small portion of CS₂^{*} is oxidized with O₂ to produce COS and SO₂ during the pseudo-steady state process of continuous CS₂ photo excitation reaction and CS₂^{*} quenching reaction. In addition, the solar flux spectrum in the troposphere is strong enough to trigger the above CS₂ photochemistry.

In this study, an updated CS₂ photochemical network is studied by a 1-D atmospheric photochemical model (PATMO). Reaction path analysis is carried out using an open-source reaction network viewer (ReNView). From the simulated result, major reduced sulfur species (CS₂, COS and SO₂) reproduce field measurements. When the zenith angle of sunlight is 0°, our result shows that the conversion ratio of CS₂ to COS is 0.87. The reaction rate *r* for the net CS₂ photo-induced oxidation and CS₂ + OH reactions at 1 km are about 18 and 144 molecule cm⁻³ s⁻¹ respectively. These results indicate that, under favorable light conditions photochemistry is a relevant tropospheric sink of CS₂.

References

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