

## **B-3 Chemistry of the Tropospheric Trace Gases Related to Global Warming (Final Report)**

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The abundance of most trace gases in the troposphere is determined by a balance between the supply of material to the atmosphere (sources) and its removal via chemical reaction processes (sinks). Especially, recent increase of ozone in the unpolluted troposphere is important for global warming by two reasons. One is that ozone is a very effective green house gas. The other is the global importance of ozone in generating OH radicals by the photoproduction of O(<sup>1</sup>D) and its reaction with water vapor. As a source of tropospheric ozone, the importance of photochemical ozone was pointed out recently, in addition to influx of ozone from the stratosphere. Therefore, studies on gas phase chemical reactions (especially, free radical reactions) and photoabsorption and photodecomposition processes of tropospheric trace gases, and measurements of ozone and other trace gases, such as NO<sub>x</sub> and hydrocarbons, in clean air sites are important to elucidate global warming processes.

In this research program, three group studies were carried out:

- (1) Measurements of rate constants and mechanisms of free radical reactions related to tropospheric trace gases : Two types of studies were carried out in order to understand chemical processes among tropospheric trace gases. 1) Determination of rate constants and reaction mechanisms of free radical reactions such as RO<sub>2</sub>+NO, R+O<sub>2</sub>, HO<sub>2</sub>+O<sub>2</sub>, were studied by the use of photoionization mass spectrometer and more than 10 new rate constants were determined and reported. 2) Photooxidation of natural hydrocarbons and estimate of global CO budget : OH radical - initiated photooxidation of terpenes and isoprene was investigated experimentally by a 6-m<sup>3</sup> photochemical reaction chamber. Reaction products were measured by a long path FTIR spectrometer. Global annual CO yields in the real atmosphere were evaluated.
- (2) Studies to evaluate budget of atmospheric trace gases : Photoabsorption cross-section of atmospheric trace gases, such as N<sub>2</sub>O and seven selected CFC's are measured using a combination of VUV monochromator and synchrotron orbital radiation. IR - UV two photon laser induced fluorescence technique was developed in order to detect OH radicals in the atmosphere.
- (3) Studies on the increase of ozone in the troposphere : Air craft observations of ozone in the troposphere were carried out in Japan, east Siberia and Japan Sea. In addition to ozone, NO<sub>x</sub> and other trace gases were measured. Chemical reaction model calculation was done to estimate the natural background level of ozone. Quantitative considerations of the trend of ozone in the troposphere was discussed.