

B-4 Clarification of the Atmospheric Chemistry of GHGs and Related Compounds

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The concentration of most trace gases in the atmosphere is determined by balance between the supply of the gases to the atmosphere (sources) and their removal via chemical and biochemical transformation processes (sinks). Particularly, the removal via chemical processes is important and the major part of atmospheric chemistry.

The followings are the objectives of this research project.

- (1). Photooxidation mechanisms of trace gases initiated by hydroxyl radicals, and ozone: High reactivity of the OH radical with a wide range of species leads to oxidation and chemical conversion of most trace gases that have appreciable physical lifetimes in the troposphere. Analysis of reaction products by photooxidation is important to understand the mechanism of free radical chain reactions in photooxidation.
- (2). Determination of the rate constants for elementary reactions concerning to free radicals: In order to clarify the radical-chain processes in the atmosphere, information on rate constants for each elementary reaction is required, especially for setting up chemical models of the atmospheric chemistry.
- (3). Determination of photodissociation rate of trace gases: Measurement of absorption cross sections and that of quantum yields of photodissociation products are necessary to estimate removal rates of trace gases and formation rates of free radicals.

The main results obtained are as follows

- (1). OH radical-initiated photooxidation of isoprene and α -pinene have been investigated experimentally by a 6-m³ photochemical reaction chamber equipped with a long path length FTIR spectrometer. The CO yield in the real atmosphere was evaluated as 39 % on the carbon number basis and global annual CO production from isoprene was estimated to be 133 Tg C yr⁻¹. Together with the estimate of the CO production from terpenes, global CO production from natural hydrocarbons was evaluated to be 229 Tg C yr⁻¹.
- (2) The rate constant for the important reaction, CH₃O₂ + NO → CH₃O + NO, was determined by the photoionization mass spectrometry. The rate constant determined was $(11.2 \pm 2.4) \times 10^{-12} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$, which is 50 % larger than the IUPAC recommended value. The rate constant for HO₂ + NO → OH + NO₂ was also determined.
- (3) The HOCO radical has been successfully detected by a photoionization mass spectrometry in gas phase. A tunneling dissociation of HOCO to H + CO₂, which implies the importance of the tunneling in the OH + CO reaction was observed. The rate of reaction of HOCO radical with molecular oxygen has also been determined, and appeared pressure-independent.