

B-4.1 STUDIES ON PHOTOCHEMICAL REACTION MECHANISM OF GREENHOUSE GASES AND RELATED GASES IN THE ATMOSPHERE

Contact Person Nobuaki Washida
Director, Atmospheric Environmental Division
National Institute for Environmental Studies
Environmental Agency
16-2 Onogawa, Tsukuba, Ibaraki 305 Japan
Phone +81-298-51-6111(Ext.350), Fax +81-298-51-4732

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Abstract For the purpose of obtaining the basic data to estimate the emission rate of CO from the photooxidation of natural hydrocarbons terpenes in the atmosphere, OH radical-initiated photooxidation of isoprene and terpenes have been investigated experimentally by a 6-m³ photochemical reaction chamber equipped with a long path length FTIR spectrometer. In the absence of NO_x, the reaction mechanism was found to be quite different from that in the presence of NO_x and major reaction products appeared in the infrared spectra were attributed to organic hydroperoxides. The CO yield from the reaction of OH with isoprene 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. Gross annual emission of CO from the reactions of OH with terpenes was estimated to be 22 Tg C yr⁻¹ (50 Tg CO yr⁻¹) by regarding α -pinene as the representative terpenes. The ultimate yield of CO from the tropospheric oxidation of terpenes (including both ozone and OH reactions) was estimated to be 20 % on the carbon number basis, and the total annual emission of CO was evaluated to be 96 Tg C yr⁻¹ (222 Tg CO yr⁻¹). In consequence, global CO production from natural hydrocarbons was evaluated to be 229 Tg C yr⁻¹.

1.BACKGROUND

The continuous increase of atmospheric trace gases such as methane, nitrous oxide, CFCs, and tropospheric ozone, has been reported and their potential role in the global warming has been alerted. However, the cause of the increase is not straightforward because the concentration of atmospheric trace gases is controlled by a critical balance of their sources and sinks which are less understood. An improved knowledge on the photochemical reaction processes in the atmosphere is needed since they play important role in sources and sinks of the greenhouse gases.

2.OBJECTIVES

The goal of this research project is to elucidate the following photochemical reaction mechanisms experimentally with use of a photochemical reaction chamber.

(1)Photochemical process related to CO budget, photooxidation of natural hydrocarbons

Carbon monoxide (CO) is a key species in tropospheric chemistry because its reaction with hydroxyl (OH) radical controls the tropospheric concentration of OH radicals which determines the atmospheric lifetime of a greenhouse gas, methane, as well as other hydrocarbons in the atmosphere. The growth of fossil fuel combustion, which simultaneously emits CO with CO₂, has been speculated to affect the tropospheric OH radical concentration. However, this must be carefully investigated in view of tropospheric CO

budget. Several estimates show that a major (>50%) CO source is photooxidation of hydrocarbons which consist of methane (~50%) and natural hydrocarbons (>40%). Therefore, the photooxidation mechanism of natural hydrocarbons is important in establishing the CO budget, but has been poorly understood. In this research project, photooxidation mechanism of natural hydrocarbons, isoprene, and terpenes, is experimentally investigated under the conditions of natural atmosphere.

(2) Photochemical degradation mechanism of HCFCs and HFCs

HCFCs (hydrochlorofluorocarbons) and HFCs (hydrofluorocarbons) are now being brought into use as CFC alternatives. These compounds contain hydrogen atoms and are believed to be short-lived in the atmosphere due to its fast reaction with OH radicals. However, a great care must be taken for their potential danger in the effect on tropospheric chemistry (especially in the secondary greenhouse effect) because the photochemical degradation mechanism of these compounds has been poorly elucidated. In this research project, the photooxidation mechanism of selected HCFCs and HFCs is investigated.

3. RESULTS

(1) Photooxidation of natural hydrocarbons; mechanism and CO yield

Since the photooxidation mechanism is expected to depend largely on the concentration of NO_x, mechanism and CO yield were investigated under two limiting conditions, i.e. with high NO_x concentration and without NO_x, and CO yield was evaluated by interpolation of two limiting cases. In chamber experiments for the photooxidation of isoprene, the OH radicals were produced by the photolysis of hydrogen peroxide (H₂O₂).

(a) Under high NO_x concentration: Identified primary photochemical reaction products and yields were: methyl ketone (MVK), 30 ± 4 %; methacrolein (MA) 21 ± 1 %; and formaldehyde (FA), 54 ± 5 %. Unidentified products (50 %) were considered to be carbonyl compounds and organic nitrates. The CO yield was determined as 51 % C. Considering the effect of photolysis and inhomogeneous reaction in the real atmosphere, CO yield was evaluated as 50 %.

(b) Under NO_x free condition: Under high concentration of isoprene, same products observed under high NO_x concentration (MVK, MA, FA) were identified. However these products yields decrease and approach to zero when the ratio [isoprene]₀/[H₂O₂] was decreased (see Fig.1). The products MVK, MA, and FA were observed due to the mutual reactions of RO₂ radicals, which are unimportant under the condition of real atmosphere. Thus the mechanism and CO yield were investigated under low [isoprene]₀/[H₂O₂] conditions. Under these conditions main photo-oxidation products were hydroperoxides, and CO yield was 23 % C. Correction for the inhomogeneous reactions in the real atmosphere were made and CO yield was evaluated as 10 %.

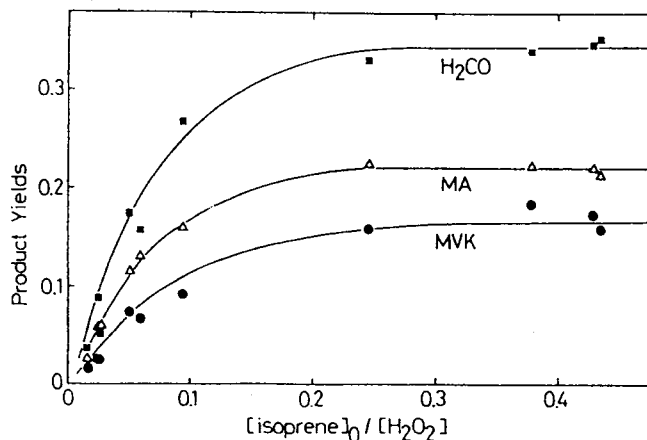


Fig. 1. Variation of product yields with initial condition ($[isoprene]_0/[H_2O_2]$) under NO_x free condition

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. (c)CO yield from the atmospheric oxidation of terpenes: α -Pinene have been estimated to be consumed by OH and ozone in a ratio of 30 : 70. Total annual emission of terpenes was reported to be 480 Tg C yr⁻¹. 30 % of α -pinene is consumed by OH and the yield of CO from OH reactions is 15 %. Thus gross annual emission of CO from the reactions of OH with terpenes was estimated to be 22 Tg C yr⁻¹ (50 Tg CO yr⁻¹) by regarding α -pinene as the representative of terpenes. The yield of CO via ozone reactions was found to be 15.4 % and the annual emission of CO via this reactions was estimated to be 74 Tg C yr⁻¹. Then, the total annual emission of CO is 96 Tg C yr⁻¹ based on the atmospheric oxidation of terpenes including both ozone and OH reactions.

The global annual CO production from the tropospheric oxidation of natural hydrocarbons (isoprene and terpenes) was evaluated to be 229 Tg C yr⁻¹, which agrees with a previous estimation.(see Table 1).

TABLE 1. An Estimate of Annual CO Production from Natural Hydrocarbons

Hydrocarbon	Annual Emission ¹⁾ (Tg C yr ⁻¹)	CO Emission (Tg C yr ⁻¹)
Isoprene	350	133
Terpenes	480	96
Total		229
	(previous estimate ²⁾	240)

1) Zimmerman et al., Geophys. Res. Lett. 5, 679 (1978)

2) Logan et al., J. Geophys. Res. 86, 7210 (1981)

(2)Photochemical degradation mechanism of HCFCs and HFCs

Photochemical degradation mechanism of HCFCs and HFCs has been studied. The primary photooxidation products (mainly carboxylic acid chlorides) were identified and their yields were determined. Compounds containing larger number of chlorine atoms were found to produce C-C bond cleavage products (CCl₂O and CX₂O) with higher yields. The major degradation products of HFCs observed were CF₃COF, CF₂O, CHFO, CF₃OOOCF₃, CO, and CO₂. These degradation mechanisms of HFCs vary from compound to compound, and depend on the number and the location of the F atoms in HFC molecules.