A-3.2 Studies on Photochemical Reactions Related to Stratospheric Ozone Depletion

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Total Budget for FY1990-Fy1992 23,928,000 Yen

Abstract

In order to make clear the detailed mechanism of ozone depletion by CFCs and orher compounds, simulation experiments of the ozone loss by the addition of halocarbons have been performed by using a photochemical reaction chamber. The loss rates of ozone by CFCs , halons, and HCFCs were determined. The mechanisms of ozone depleatin by CFC and halon were discussed. Synergetic effect of halon on ozone depletion by CFC was first demonstrated experimentally. The rates of radical reactions related to ozone loss in the stratosphere have been measured by using a laser photolysis-photoionization mass spectrometry. The rate constant for rection of CCl_3+O_3 was first determined to be $(9.0 \pm 0.8) \times 10^{-13}$ $cm^3 molecule^{-1}$ s^{-1} at room temperature. It has been estimated that the reaction with ozone slightly contributed (<0.03%) to the fate of CCl_3 radicals in the stratosphere.

Key Words Photochemical Chamber, Simulation Experiment, Photoionization Mass Spectrometry, Reaction Rate Constant

1.Introduction

Our understanding of chemical reactions related to stratospheric ozone depletion has been accumulated since a potential threat of human activeties to the ozone was pointed out in the early 1970's, and it has become possible to evaluate effects of the human activities on the ozone by numerical models which include the chemistry in the stratosphere. However, current models can neither simulate the ozone distribution around 40 km altitude nor predict decreasing trend in total ozone at middle latitude in springtime. This indicates our understanding of the chemistry in the stratosphere is not yet sufficient to predict the change in the stratospheric ozone properly. Therefore, it is necessary to increase our knowledge and improve our understanding of the chemistry in the stratosphere in detail.

2.Objectives

In this research project, major objectives are (1) to make clear the detailed mechanism of ozone depletion by CFCs and other compounds by laboratory experiments, and (2) to get kinetic information on radical reactions related to ozone loss in the stratosphere. In the first objective, simulation experiments of ozone depletion by CFCs, halons, and other potential substances have been performed by use of a stratospheric photochemical reaction chamber (abbreviated as photochemical chamber). In the second objective, elementary chemical reactions which are not well understood of their reaction rates and/or products have been studied by use of a photoionization mass spectrometry.

3.Simulation Experiments of Ozone Depletion by Halocarbons

Simulation experiments of ozone depletion by the addition of selected CFCs, halons, and hydrogen-substituted halocarbons were performed by use of a photochemical chamber. Synergetic effect of halon (BrOx chemistry) on ozone depletion by CFC (ClOx chemistry)

which had been proposed to explain the ozone loss especially in the polar region was first demonstrated experimentally.

(i) Experimental

The photochemical chamber is equipped with a stratospheric solar simulator which can provide a radiation with enhanced flux in the ultra-violet region similar to the solar radiation in the mid-altitude stratosphere. Irradiation of the solar simulator to purified air of 50 Torr (corresponding to the atmospheric pressure at ca. 20 km altitude in the stratosphere) in the chamber can give a photochemical steady state of ozone. After the photochemical steady state of ozone having been established, calculated amount of CFC and/or halon were introduced into the chamber. Decay of ozone was monitored by UV absorption at 253.7 nm. Reactants and products were monitored, if necessary, by in-situ FTIR measurements with 220 nm optical path-length in the chamber.

(ii) Results and Discussion

(a) *Ozone Depletion by CFCs, halons, and hydorgen-substituted halocarbons*

The addition of CFC, halon, or hydrogen-substituted halocarbon to the mixture of a photochemical steady state of ozone with purified air caused effective depletion of ozone. As an example, the decay profile of ozone by the addition of CFC-11 ($CFCl_3$) of 5.8 ppm is shown in Fig. 1(a). The ozone loss rate, $k(O_3)$, by the photolysis of CFC-11 was defined as the slope of the decay curve averaged from the beginning of the decay till a half value of the initial concetration, as shown in the figure. $k(O_3)$ value by CFC-11 was determined to be 75 ppb/min in this case. From the concetration of CFC-11 added and the photodecomposition rate of CFC-11 (7.32×10^{-4} min^{-1}), the photodecomposition loss rate, kx, of CFC-11 was calculated to be 4.2 ppb/min. The $k(O_3)/kx$ ratio was used as an indicator of the efficiency of ozone depletion. Hereafter, the $k(O_3)/kx$ ratios for CFCs, halons, and others were determined as relative values to that for CFC-11 and are summarized in Table 1.

Table 1. Relative Ozone Depletion efficiency by CFCs, halons, and HCFCs.

CFC		halon		HCFC	
CFC-11* ($CFCl_3$)	1	H-1301 (CF_3Br)	1.7	HCFC-141b (CH_3CFCl_2)	1.0
CFC-12 (CF_2Cl_2)	1.0	H-2402 ($C_2F_4Br_2$)	2.8	HCFC-123 (CF_3CHCl_2)	0.5
				HCFC-124 (CF_3CHFCl)	0.5

* reference molecule

As seen from Table 1, halon has been found to reduce the concentration of ozone more efficiently than CFC under our experimental condition. Ozone decay rate was thought to depend on the rate of the reproduction of halogen atoms (Cl or Br). In order to clarify the mechanism of ozone loss by CFC and halon, numerical calculation using a chemical reaction model was performed. The model calculation for our simulation experiments suggests that the mutual radical-radical reaction of BrO + BrO play an important role for the reproduction of Br atoms. On the other hand, the reaction of ClO + ClO generates rather ClOOCl molecules. Furthermore, it is suggested that the photolysis of ClO radicals is important to reproduce Cl atoms, which cannot constitute effective ozone loss cycles.

Therefore, the difference of ozone depletion efficiency between CFC and halon is thought to be explained in terms of the defference in reproduction mechanism of halogen atoms. The photolysis of HCFC-141b(CH_3CFCl_2) decayed ozone as fast as CFC-11. Contrary to HCFC-141b, HCFC-123(CF_3CHCl_2) and HCFC-124(CF_3CHFCl) decomposed ozone with a half efficiency of HCFC-141b. Number of Cl atoms included are different among HCFCs: two Cl atoms for HCFC-141b and 123 and one for HCFC-124. This suggests that the efficiency of ozone depletion by HCFCs depends on the efficiency of Cl release through photochemical reactions of related radicals.

(b) *Synergetic Effect of Halon on Ozone Depletion by CFC*

Figures 1(a) and (b) show the ozone decay profiles observed in the CFC-11 (5.8 ppm)/O3/air and halon-1301 (1.95 ppm)/O3/air systems, respectively. The decay profile taken when both CFC-11 (5.8 ppm) and halon-1301 (1.95 ppm) were introduced simultaniously into the chamber is shown in Fig. 1(c). As shown in Fig. 1, the decay of ozone by the co-addition of both halogen compounds became faster and the loss rate of ozone (121 ppb/min) was higher than the sum of that by the addition of CFC (75 ppb/min) or halon (36 ppb/min) separately. This result experimentally demonstrates the supposed synergetic effect of halon on the ozone depletion by CFC, which could be explained in terms the effective reproduction of haloge atoms by the radical-radical reaction of BrO+ClO.

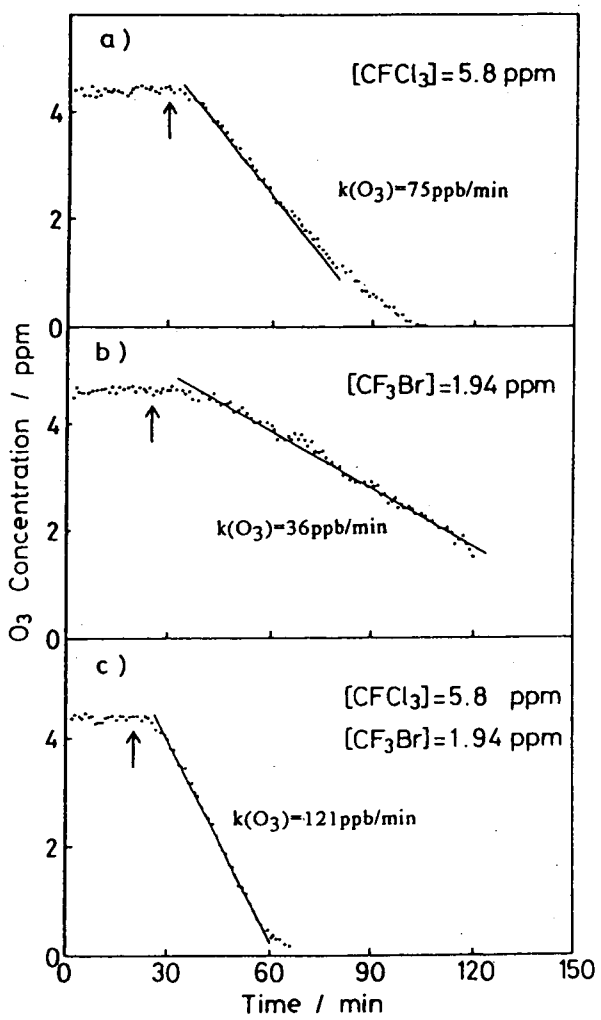

Fig.1.Decay of ozone when (a) CFC-11, (b) halon-1301 and (c) CFC-11+halon-1301 were added.

4. Rate Constant for Reaction of CCl_3+O_3

The ultraviolet photolysis of halomethane (CX_4: X=F or Cl) in the stratosphere produces Cl atoms and related halomethyl radicals (CX_3). The reaction rate constants of CX_3 radicals with O_2 were measured by a photoionization mass spectrometry. The reaction rate constant of CCl_3+O_2 was found to be smaller than those for other reactions of CX_3+O_2. If the rate constant for reaction of CCl_3+O_3 is sufficiently large (i.e. $\sim 10^{-10}$ $cm^3 molecule^{-1} s^{-1}$), the reaction with ozone can not be excluded for the fate of the CCl_3 radicals in the stratosphere. However, no information on reaction rates of CCl_3+O_3 has been available. In this work, the rate constant for reaction of CCl_3+O_3 was determined.

(i) Experimental

The gas mixture of $CCl_4/O_3/O_2$ diluted in N_2 was flowed through a Pyrex tubular reactor and was coaxially irradiated by a 193 nm ArF excimer laser to generate the CCl_3 radicals. CCl_3 was sampled through a thin pinhole (ϕ=0.3mm) on the wall of the reactor and was photoionized using a Kr resonance lamp with a MgF_2 window (10.03 and 10.64 eV) powered by microwave discharge. The parent ions of the radicals (CCl_3^+) were mass-selected by a quadrupole mass filter and were detected with a Daly type scintillation ion detector.

Ozone was generated by flowing O_2 through a commercal ozonizer. Concentration of ozone was monitored by a UV-absorption spectrometry at 253.7 nm. All experiments were carried out at room temperature.

(ii) Results and Disscussion

Figure 2 shows the decay profile of CCl_3 taken in the $CCl_3/O_3/O_2$ system. The dashed line in the figure represents the decay curve observed when O_3 was converted to O_2 by passing through the heated quartz tube. The decay rate for reaction of CCl_3+O_3 was calculated from a difference in total removal rates of CCl_3 measured with and without O_3. The increase of the partial pressure of O_2 by the conversion of O_3 to O_2 was taken into account. From the plots of the decay rates against the partial pressure of O_3, the absolute rate constant for reaction of CCl_3+O_3 was determined to be $(9.0\pm 0.8)\times10^{-13}$ $cm^3molecule^{-1}s^{-1}$. By using reaction rate constants obtained in this project, it has been estimated that the reaction with O_3 slightly contributes (<0.03%) to the fate of the CCl_3 radicals in the stratosphere.

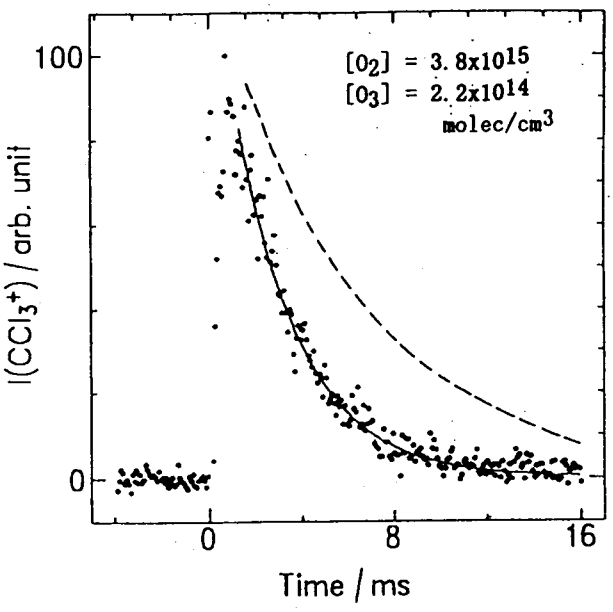

Fig.2. Typical profiles of $CCl3^+$ ion signals taken with (····) and without (---) ozone.