Effect of Increasing CO_2 on the Stratospheric Level of CO and O_3

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Received April 25, 1988

ABSTRACT

Production and destruction processes of carbon monoxide (CO) and ozone (O_3) are examined in the light of increasing amount of atmospheric carbon dioxide (CO_2). It is found that doubling of CO_2 will increase the stratospheric concentration of CO and will have positive effect on O_3 concentration.

I. INTRODUCTION

Photochemistry alone contributes 70% of the global CO production and 80% of the global CO destruction (Seiler, and Warneck, 1972). It is transported in the lower stratosphere through diffusion process from troposphere where it is produced by natural as well as anthropogenic sources. In the upper stratosphere photodissociation of carbon dioxide (CO_2) is an important source of CO (Shimazaki and Cadle, 1973). The other product of photodissociation of CO_2 is atomic oxygen (O) which is the key element in the only established production mechanism of O_3 i.e. $O+O_2+M \rightarrow O_3+M$. Although production of O through photodissociation of CO_2 is far less than through photodissociation of O_2 in the mesosphere and lower thermosphere or through O_3 in the stratosphere, however, it is not known whether it can be neglected safely. Groves and Tuck (1980) have studied the effect of increasing atmospheric CO_2 on the O_3 concentration by employing one dimensional photochemical radiative model. They suggested that increase in CO_2 concentration resulting in cooling of the upper stratosphere would increase the concentration of O_3. Present study is an attempt to examine some aspects of the possible effect of increasing CO_2 concentration on the stratospheric CO and O_3 concentration.

II. RESULTS AND DISCUSSION

Recently available data on solar spectral irradiance, photoabsorption cross section and chemical reaction rate coefficient compiled by Deshpande and Mitra (1983) and Shimazaki (1985) have been adopted to calculate CO_2 dissociation rate (J) and various chemical reaction rates (R). Same formula is adopted as it was used in the earlier studies by author (Hingane, 1978). CO_2 dissociate mainly in the ultraviolet (UV) spectral region (0.116 to 0.195 μm) where molecular oxygen has strong absorption bands, therefore attenuation due to molecular oxygen absorption is accounted. Strong dependence of CO_2 photodissociation on zenith angle and declination angle is also considered. Values of J are calculated for the two sets of mixing ratio values of CO_2 viz., 300 ppmv and 600 ppmv and the results are presented in Fig. 1. As mentioned above CO_2 absorbs solar radiation mainly in the UV spectral region, therefore its dissociation is effective only above 30 km with maximum rate around 40 km. Further, it is also seen that although the value of dissociation rate coefficient in the lower stratosphere decreases with increasing concentration of CO_2, photodissociation rate does not

decrease accordingly.

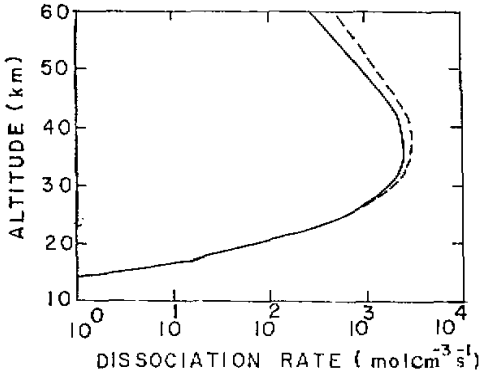

Fig. 1. Photodissociation rate of CO_2 for the two sets of mixing ratio values viz., 300 ppmv and 600 ppmv (dotted curve).

The products of photodissociation of CO_2 are CO and O. The molecules of CO produced in this process are comparatively less chemically active species in the stratosphere; it is slowly oxidized by hydroxyl molecule (OH). Calculating lifetime (τ_{CO}) of CO in this region is 10^8 to 5×10^9 seconds which is markedly high. Therefore, diffusion process plays a central role in its spatial distribution. At the same time, anthropogenic sources like incomplete combustion of hydrocarbon fuel near ground cause upward flux of CO in the lower stratosphere. The flux between troposphere and stratosphere is 1.2×10^5g S^{-1} with the assumption of 0.08 ppmv mixing ratio (Newell and Boer, 1974). Present computations show that in the whole stratosphere about 3×10^{11} grams of additional CO will be added per year due to the doubling of CO_2. This amount of CO seems to be quite less than the production due to natural source like methane and formaldehyde. However, this additional amount in the stratosphere would lead to reduction in the rate of upward transportation from troposphere to stratosphere and hence ultimately tropospheric concentration of CO would increase. The other product of CO_2 photolysis is atomic oxygen. The amount of oxygen produced in this process is less certainly more than three orders of magnitude less than that produced by molecular oxygen photolysis; however, it should be kept in mind that O produced in CO_2 photolysis is available in situ for three body recombination to produce O_3, whereas that produced due to O_2 photolysis is in the mesosphere or lower thermosphere from where it is diffusing downwards to stratosphere.

The additional amount of carbon monoxide and atomic oxygen produced due to doubling of CO_2 would be entering into the ozone chemistry as follows. The reaction between O_3 and OH is one of the major loss process of O_3 in the lower stratosphere, e.g.

$$OH + O_3 \rightarrow HO_2 + O_2$$
$$HO_2 + O_3 \rightarrow OH + 2O_2$$
$$2O_3 \rightarrow 3O_2$$

This cycle destroys two molecules of ozone. Now CO is oxidized by OH and this oxidation rate will be increased due to additional amount of CO and ultimately reduce the

availability of OH for above cycle, therefore as a result ozone loss rate will decrease. The reaction between CO and OH also initiates the series of reactions in which the following two are key reactions.

$$HO_2 + NO \rightarrow OH + NO_2$$

and $$HO_2 + O_3 \rightarrow OH + 2O_2$$

They will have an opposite effect on ozone concentration i.e. if first one is faster than second one, the net effect will be production of O_3 or otherwise (for detail please see Shimaraki, 1985). In our calculation it is seen that the first reaction is faster than the second one by about 5 times to about one order of magnitude in the troposphere and lower stratosphere and doubling of CO_2 does not show any significant effect on these cycles.

Thus, above results and discussion lead to the conclusion that increasing amount of carbon dioxide in the atmosphere will increase the concentration of carbon monoxide both in the troposphere and stratosphere and will have positive effect on ozone concentration. However, the results can be adequately quantified only after employing 1–D or 2–D photochemical diffusive model since most of the reactions involved in the destruction or production processes are strongly coupled among themselves.

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