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Origin of Nitrous Oxide in the Atmosphere

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The origin of nitrous oxide in the atmosphere is due to the reaction between nitrogen molecules and oxygen atoms formed by the photochemical dissociation of ozone in the atmosphere. The steady state of 5×10^{-7} nitrous oxide in the atmosphere is due to the photochemical equilibrium between nitrous oxide formation and nitrous oxide decomposition, the latter in the upper atmosphere.

Nitrous oxide is present in the atmosphere in a concentration of 5×10^{-7}, similar to the amount of hydrogen present but greater than the ozone content.[1] In a letter to the *Journal of Chemical Physics* we have indicated that experimentally, the following reaction (I) has been accomplished and has a heat of activation of only about 12 kcal.[2]

$$N_2+O+M=N_2O+M. \qquad \text{(I)}$$

The reason for the presence of nitrous oxide in the atmosphere, has, to date, not been explained. We believe the presence of nitrous oxide in the atmosphere to be due to a photochemical equilibrium between nitrous oxide formation and nitrous oxide decomposition, as follows:

$$O_3+h\nu_{(II)}=O_2+O, \qquad \text{(II)}$$

$$O_2+O+M=O_3+M, \qquad \text{(III)}$$

$$O_2+O+M=O_3^*+M, \qquad \text{(IIIa)}$$

$$N_2+O_3^*=N_2O+O_2, \qquad \text{(Ia)}$$

$$N_2O+h\nu_{(IV)}=N_2+O \text{ or } NO+N.^3 \qquad \text{(IV)}$$

If the sum of the light quanta absorbed by ozone is known[4,5] ($h\nu_{II}=5\times10^{15}/\text{cm}^2$ sec), the nitrous oxide production can be readily calculated, which will be, in turn, equivalent to the photochemical decomposition of nitrous oxide in the stationary state.

$$\frac{+d(N_2O)}{dt}\text{produced}=\frac{h\nu_{II}\times k_I\times(N_2)}{k_{III}\times(O_2)}$$

$$=\frac{-d(N_2O)}{dt}\text{decomposed}=h\nu_{IV}, \qquad \text{(V)}$$

with

$$k_I/k_{III}=(f)e^{-12\,000/RT};\ (N_2)/(O_2)=4;$$

$$h\nu_{II}=5\times10^{15};\ (f)=10;$$

$$\frac{+d(N_2O)}{dt}\text{produced}=5\times10^{15}\times4\times(f)\times\exp\left(\frac{-12\,000}{1.985\times300}\right)=3.5\times10^{8}.$$

k_{III} and k_I, are the reaction velocity constants for reactions (III) and (I), respectively. $h\nu_{II}$ and $h\nu_{IV}$, are the absorbed light quanta per cm²/per sec, in the daytime, for ozone and nitrous oxide, respectively. The temperature of the atmosphere ranges from 220° to 320°K, but since the higher temperatures are more effective, we have used a temperature of 300°K in these calculations.[6] The (f) factor is used to include some degrees of freedom which may be effective in reaction (V).

An evaluation of the absorption coefficients of nitrous oxide, oxygen, and ozone, shows, that only in the wavelength region of 1900A to 2050A, the nitrous oxide absorbs reasonably and is photochemically dissociated, and indicates that of the 10^{13} light quanta per cm² per sec, available from the sun's irradiation, only 10^8 to 10^9 per cm² per sec are absorbed. This result compares very favorably with that calculated in Eq. (1).

With about 10^{19} nitrous oxide molecules per cm² present in the atmosphere, the time of relaxation can be calculated as

$$10^{19}/(1.5\times10^{7}\times3\times10^{8})=2\times10^{3}\text{ years,}$$

where 1.5×10^7 is one-half the number of seconds in one year, and 3×10^8 is the number of light quanta absorbed by nitrous oxide per cm² per second. Since the concentration of nitrous oxide in water at 10°C is almost the same as in the gas phase, the nitrous oxide in the atmosphere would be washed out once in about 10^4 years.

The explanation presented above presumes that the nitrous oxide would not be attacked or be produced biologically. This question could readily be answered by an analysis of waters of different origins. We are presently investigating other possible reactions of nitrous oxide in the atmosphere, which may play a minor role, as

$$NO_2+N=N_2O+O.^7 \qquad \text{(VI)}$$

It seems that the exact knowledge of the nitrous oxide behavior [i.e., heat of activation, diffusion, separation, and (f) factor] in nature, as with carbon-14 and tritium, would enhance the finer details of the behavior of the atmosphere.

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[1] L. E. Miller, J. Chem. Educ. **31**, 112 (1954); G. P. Kuiper, *The Atmospheres of the Earth and Planets* (University of Chicago Press, Chicago, 1949).

[2] P. Harteck and S. Dondes, J. Chem. Phys. **22**, 758 (1954).

[3] Henriques, Duncan, and Noyes, J. Chem. Phys. **6**, 518 (1938).

[4] Watanabe, Inn, and Zelikoff, J. Chem. Phys. **21**, 1026 (1953); Johnson, Purcell, Tousey, and Watanabe, J. Geophys. Research **57**, 157 (1952).

[5] Zelikoff, Watanabe, and Inn, J. Chem. Phys. **21**, 1643 (1953).

[6] Reaction (IIa) considers that the formation of ozone in a three-body collision first forms an activated ozone molecule (the heat of formation being 23 kcal). Therefore, reaction (Ia) may not be neglected in comparing it with reaction (I), especially not at the lower temperatures.

[7] P. Harteck and S. Dondes, J. Chem. Phys. **22**, 953 (1954).