Reports

Ozone: Decomposition by Ionizing Radiation

Abstract. *The decomposition of ozone by ionizing radiation is explained by a negative ion-chain mechanism. That this mechanism may be pertinent is indicated by the results obtained from the irradiation of liquid oxygen and the irradiation of oxygen containing nitrogen.*

Oxygen and ozone behave quite differently when irradiated with ionizing radiation or with ultraviolet light. When oxygen is irradiated by ionizing radiation, a steady-state ozone concentration of only a few parts per million is reached, whereas with ultraviolet light concentrations as high as several percent can be obtained. On the other hand, ozone is decomposed by ionizing radiation more rapidly than by ultraviolet light by several orders of magnitude. For this much-studied antithetical behavior of oxygen and ozone to radiolysis and photolysis Fueki and Magee present an explanation. Fueki and Magee tentatively (*1*) suggested a possible ion-chain mechanism and amplified (*2*) this ion-chain mechanism as the cause for the marked difference in the radiolytic decomposition of ozone. Their overall mechanism not only includes the homogeneous gas reaction but also the inhomogeneous case where the effects of ionizing radiation are concentrated along the tracks. This latter treatment may be especially important when fission fragments are used as the source of ionizing radiation.

We too have been studying the ozone decomposition and independently conceived a similar ion-chain mechanism. We now present some aspects not covered by Fueki and Magee. The overall mechanism with the important equations is shown in Table 1. The negative ions formed in reaction III cycle over reactions IV and V, destroying ozone and regenerating negative ions, until the chain-terminating step of ion recombination, reaction VI, occurs.

First, the rate of decomposition of ozone can be calculated from the ion-chain mechanism of Table 1. For each cycle (reactions IV and V) of the chain, reaction VI should be the limiting step. The rate of this charge-transfer reaction can be estimated from the heat of activation and the collision frequency. Kircher (*3*) measured the temperature dependence of ozone formation in the irradiation of oxygen and also determined the heat of activation for the ozone-consuming process to be about 2 kcal. This can be assumed to be identical with the heat of activation for reaction IV. If one assumes a collision frequency of 1.5 × 10^{10} collisions per second, a value of 10^{-12} (particle/cm^3)$^{-1}$ sec^{-1} is obtained for the rate constant, K_4. From this value, an estimate of the time for a cycle to occur and the rate of the decomposition of ozone can be determined.

Second, if the foregoing values are applied to the irradiation of pure ozone with radon, as conducted by Lewis (*4*), with 50 mm of ozone present, a cycle would take about 10^{-7} seconds. The chain length will depend on this value and also on the lifetime of the ions consumed by reaction VI. To estimate the lifetime of the ions, we shall assume a value of the order of 10^{-7} (particle/cm^3)$^{-1}$ sec^{-1} for the ion recombination coefficient, K_6, the value usually ascribed (*5*). The rate of loss of the ions, $-dI/dt$, can then be expressed as:

$$\frac{-dI}{dt} = k_6\,(O_2^-)\,(O_2^+) \qquad (1)$$

At equilibrium, this must be equal to the rate of their formation:

$$\frac{+dI}{dt} = J\,G_{(\text{ions})} \qquad (2)$$

where J is the intensity of the radiation and $G_{(\text{ions})}$ is the number of ions produced per 100 ev. If equal concentrations of positive and negative ions are assumed:

$$k_6\,(O_2^-)^2 = J\,G_{(\text{ions})} \qquad (3)$$

or

$$(O_2^-) = \left[\frac{J\,G_{(\text{ions})}}{k_6}\right]^{1/2} \qquad (4)$$

The lifetime of the ion (τ) can be expressed as:

$$\tau = \frac{(O_2^-)}{J\,G_{(\text{ions})}} = \left[\frac{1}{k_6\,J\,G_{(\text{ions})}}\right]^{1/2} \qquad (5)$$

Thus, if other conditions remain fixed, the number of ozone molecules destroyed per ion pair should be dependent only upon the lifetime of the ion, τ, which is proportional to the inverse square root of the radiation intensity. Unfortunately, Lewis did not record the exact radiation intensity he used,

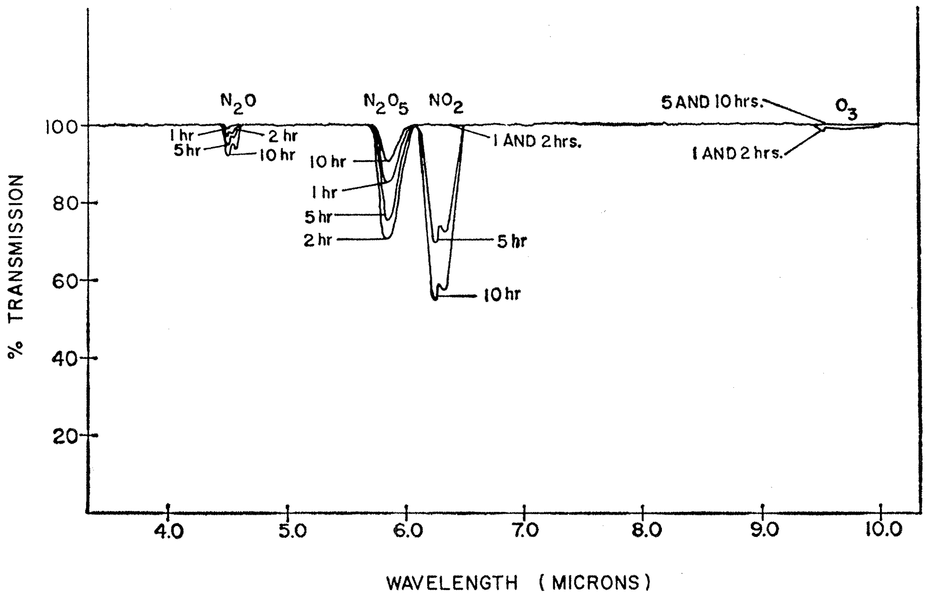

Fig. 1. Infrared spectra of products resulting from the polonium-210 irradiation of air.

Table 1. Principal ion-molecule reactions in the mechanism for ozone decomposition by ionizing radiation.

$O_3 \rightsquigarrow O_3^+ + e^-$	Ia
$\rightsquigarrow O_3^* \rightarrow O_2 + O$	Ib
$O_2 \rightsquigarrow O_2^+ + e^-$	IIa
$\rightsquigarrow O_2^* \rightarrow O + O$	IIb
$O_2 + e^- + M \rightarrow O_2^- + M$	IIIa
$O_3 + e^- + M \rightarrow O_3^- + M$	IIIb
$O_3 + O_2^- \rightarrow O_2 + O_3^-$	IV
$O_3^- + O_3 \rightarrow O_2 + O_2 + O_2^-$	V
$O_2^- + O_2^+ \rightarrow O_2 + O + O$	VIa
$O_2^+ + O_3^- \rightarrow O_2 + O_2 + O$	VIb

but from the general knowledge of the intensities used in radon experiments in that period, we may estimate a value for $J\,G_{(\text{ions})}$ of $\sim 10^{15}$ ion pairs per cubic centimeter per second. The ion lifetime at this intensity is therefore 10^{-4} second. Combining this value with that of the time for a cycle shows that more than 2000 ozone molecules should be destroyed per ion pair formed. Considering all the uncertainties in the calculations, the agreement with Lewis' value of 4500 is good.

Third, additional evidence for the importance of the ion mechanism is provided by data on the irradiation of liquid oxygen (*6*). Owing to the cage effect, the lifetime of the ions generated in the liquid phase will be much shorter than in the gas phase, and therefore the process should be less effective in decomposing ozone. Also, a small heat of activation will have a strong inhibiting effect at liquid oxygen temperature. Therefore, *G*-values for ozone formation as large as 15 should be obtained and indeed have been obtained (*6*).

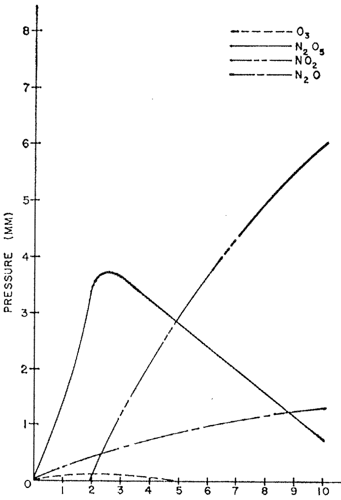

Fig. 2. Change of product concentration in the polonium-210 irradiation of air.

Fourth, there should be methods of breaking the ion-chain mechanism (*7*). One would expect that adding nitrogen dioxide, which has a higher electron affinity than ozone (*5*), to the system would break the negative ion chain by charge transfer:

$$O_3^- + NO_2 \rightarrow O_3 + NO_2^- \qquad \text{VII}$$
$$O_2^- + NO_2 \rightarrow O_2 + NO_2^- \qquad \text{VIII}$$

and result in an increased ozone concentration. Very low concentrations of nitrogen dioxide (parts per million) should be sufficient to break the chain. The results of one group of our continuing series of experiments on the radiolysis of nitrogen-oxygen mixtures show this chain breaking is a possibility. Nitrogen-oxygen mixtures (including air) were irradiated with a Po^{210} alpha source, and the gas mixture was examined continuously during the irradiation with an infrared spectrophotometer. Absorption bands of ozone, nitrogen pentoxide, nitrogen dioxide, and nitrous oxide could be observed, and from their intensities the concentrations of these gases were determined. Most strikingly, in the first 2 hours of irradiation, the ozone concentration was higher by several orders of magnitude than the few parts per million observed in the irradiation of pure oxygen (Figs. 1 and 2). This high concentration of ozone remained even though ozone is consumed to oxidize the nitric oxide and nitrogen dioxide to nitrogen pentoxide, clear evidence thus being provided that the nitrogen oxides do break the ion chain which decomposes ozone.

Unfortunately, as the irradiation proceeds, the simultaneous process of ozone removal by the oxidation of the nitrogen oxides and the thermal decomposition of nitrogen pentoxide result in a net increase in the nitrogen dioxide concentration to the point where the reaction:

$$NO_2 + O \rightarrow NO + O_2 \qquad \text{IX}$$

predominates the formation of ozone:

$$O_2 + O + M \rightarrow O_3 + M \qquad \text{X}$$

Figs. 1 and 2 show the change in the various concentrations with time. The reactions involved have been discussed in detail (*8*).

Thus, even though the nitrogen dioxide can break the negative ion chain that decomposes ozone, the nitrogen dioxide inhibits ozone formation by reacting with oxygen atoms or being oxidized to nitrogen pentoxide. Although interesting from a theoretical viewpoint, the use of nitrogen dioxide is not a means of substantially increasing the ozone concentration.

In conclusion, we have shown that the rate of the decomposition of ozone can be calculated by the ion-chain mechanism of Fueki and Magee. We have also shown that the ion-chain mechanism can be broken by adding a substance with a very high electron affinity. Our initial choice of nitrogen dioxide, while meeting these conditions, was not ideal, because nitrogen dioxide reacts with ozone and oxygen atoms. Therefore, any economical production of ozone from oxygen with strong ionizing radiation sources must involve methods of breaking the ion chain while avoiding other complicating reactions.

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References and Notes

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7. It would be most advantageous if the ozone decomposition proceeded via negative ions only, as concluded by Fueki and Magee. Because of the large uncertainties in the values reported for the ionization potential of ozone, it may be possible that ozone has a lower ionization potential than oxygen and therefore a positive ion chain cannot be excluded.
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Cosmic X-ray Sources

Abstract. *Eight new sources of cosmic x-rays were detected by two Aerobee surveys in 1964. One source, from Sagittarius, is close to the galactic center, and the other, from Ophiuchus, may coincide with Kepler's 1604 supernova. All the x-ray sources are fairly close to the galactic plane.*

Reports of the detection of cosmic x-ray sources with rocket-borne instrumentation have been published (*1–3*). Giacconi, Gursky, Paolini, and Rossi (*1*) obtained the first positive evidence of cosmic x-rays in June 1962. Their instrumentation was designed to survey a broad field of view, and the source of emission was identified with the general