Ionic Processes in the Radiolysis of Nitrous Oxide

Satoshi TAKAO, Shoji SHIDA, Yoshihiko HATANO and Hideo YAMAZAKI

Laboratory of Physical Chemistry, Tokyo Institute of Technology, Meguro-ku, Tokyo

(Received June 14, 1968)

Although many studies have been made of the gas-phase radiolysis of nitrous oxide,[1] almost nothing definite has yet been established about its mechanism. In the present study SF_6 and CO_2 were used as electron scavengers, and various rare gases, as electron suppliers.

The irradiations were done with ^{60}Co-γ rays at 25°C to a total dose of 7.2×10^{20} eV·g^{-1}. The products, N_2 and O_2, were analyzed by gas chromatography, and the amounts of NO were calculated stoichiometrically.

The observed G-values of the products of the radiolysis of pure N_2O at 50—400 mmHg were $G(N_2)=10.1$, $G(O_2)=3.8$, and $G(NO)=5.1$, independent of the pressure. On the addition of only 0.01% SF_6 to the N_2O at 200 mmHg, these G-values all decreased rapidly, they then remained constant on the further addition of up to at least 0.3%. The decreases were $-\Delta G(N_2)=2.1$, $-\Delta G(O_2)=0.6$ and $-\Delta G(NO)=1.8$; accordingly, $-\Delta G(N_2O)=3.0$. The experiments with CO_2 gave similar results, except for a much slower leveling off of the G-values.

When increasing amounts (up to 600 mmHg) of rare gases were added to N_2O of a constant pressure of 60 mmHg, the amounts of N_2, O_2, and NO, all increased linearly in the case of He and Ne, while in the case of Ar, Kr, and Xe, although N_2 and O_2 increased linearly, NO did not appreciably increase at all. The increases in the G-values of the product by sensitization, G_{sens}, based on the energy absorbed by the rare gases, are shown in Table 1.

TABLE 1. G_{sens} FOR VARIOUS RARE GASES

	G_{sens}				
	He	Ne	Ar	Kr	Xe
N_2	7.3	6.3	3.0	2.9	3.8
O_2	2.8	2.4	1.5	1.6	1.8
NO	3.0	3.2	~0.0	~0.5	~0.5

If it is assumed that all electrons are scavenged by SF_6, and that SF_6^- does not contribute in any way to the decomposition of N_2O, one may infer from the above $-\Delta G$-values and with $W(N_2O)=33.0$ eV that one electron produced by the ionization of N_2O decomposes just one molecule of N_2O and yields 0.7 molecule of N_2. In the rare-gas experiments, the charge transfer from Xe^+ to N_2O is energetically impossible, and that from Kr^+ and Ar^+ appears not to occur either in spite of their higher ionization potentials than that of N_2O (12.9 eV), for their G_{sens} values are rather similar to those of Xe. As may be seen from the G_{sens} values, one excess (excess with respect to the positive ion produced by the ionization of N_2O) electron from these three rare gases, either as itself or through neutralization, decomposes one or less molecule of N_2O and yields one or less molecule of N_2. In the cases of He and Ne, the G_{sens} are remarkably higher than those for the other rare gases, and the ionization of N_2O by charge transfer and excitation transfer surely occurs. The fact that the formation of NO is not appreciably sensitized by Xe, Kr, and Ar indicates that N_2O^+ is necessary for the formation of NO. The results obtained here can not be accounted for by the often-assumed mechanism[2];

$$e^- + N_2O \rightarrow N_2 + O^-$$

$$O^- + N_2O \rightarrow N_2 + O_2^- \text{ and } NO + NO^-$$

because, according to this mechanism, more than one molecule of N_2 should be produced per electron. In order to explain the observed fact that one electron produces one or less molecule of N_2, one must assume the long-lived N_2O^- suggested by Freeman.[3] Recently Warman[4] has also obtained evidence for the initial formation of N_2O^- upon electron capture by N_2O. Thus, the major reaction may be tentatively described as follows:

$$e^- + N_2O \xrightarrow{M} N_2O^-$$

$$N_2O^- + N_2O^+ \rightarrow N_2 + O + N_2O$$

$$\text{and } N + NO + N_2O$$

followed by the combination of O and N to form O_2 and NO through NO_2. For the final conclusion to be attained, however, more supporting evidences are required.

1) For example, F. T. Jones and T. J. Sworski, *J. Phys. Chem.*, **70**, 1546 (1966).

2) For example, J. M. Warman, *Nature*, **213**, 381 (1967).

3) W. J. Holtslander and G. R. Freeman, *J. Phys. Chem.*, **71**, 2562 (1967).

4) J. M. Warman, private communication.