

Ionic Processes in the Radiolysis of Nitrous Oxide

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(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 SF₆ and CO₂ were used as electron scavengers, and various rare gases, as electron suppliers.

The irradiations were done with ⁶⁰Co-γ rays at 25°C to a total dose of 7.2×10^{20} eV·g⁻¹. The products, N₂ and O₂, 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 N₂O at 50–400 mmHg were *G*(N₂)=10.1, *G*(O₂)=3.8, and *G*(NO)=5.1, independent of the pressure. On the addition of only 0.01% SF₆ to the N₂O 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 $-\Delta G(\text{N}_2)=2.1$, $-\Delta G(\text{O}_2)=0.6$ and $-\Delta G(\text{NO})=1.8$; accordingly, $-\Delta G(\text{N}_2\text{O})=3.0$. The experiments with CO₂ gave similar results, except for a much slower leveling off of the *G*-values.

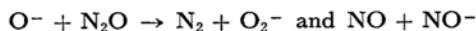
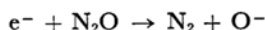
When increasing amounts (up to 600 mmHg) of rare gases were added to N₂O of a constant pressure of 60 mmHg, the amounts of N₂, O₂, and NO, all increased linearly in the case of He and Ne, while in the case of Ar, Kr, and Xe, although N₂ and O₂ increased linearly, NO did not appreciably increase at all. 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

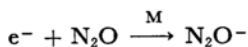
	<i>G</i> _{sens}				
	He	Ne	Ar	Kr	Xe
N ₂	7.3	6.3	3.0	2.9	3.8
O ₂	2.8	2.4	1.5	1.6	1.8
NO	3.0	3.2	~0.0	~0.5	~0.5

If it is assumed that all electrons are scavenged by SF₆, and that SF₆⁻ does not contribute in any way to the decomposition of N₂O, one may infer from the above $-\Delta G$ -values and with $W(\text{N}_2\text{O})=$

33.0 eV that one electron produced by the ionization of N₂O decomposes just one molecule of N₂O and yields 0.7 molecule of N₂. In the rare-gas experiments, the charge transfer from Xe⁺ to N₂O is energetically impossible, and that from Kr⁺ and Ar⁺ appears not to occur either in spite of their higher ionization potentials than that of N₂O (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 N₂O) electron from these three rare gases, either as itself or through neutralization, decomposes one or less molecule of N₂O and yields one or less molecule of N₂. In the cases of He and Ne, the *G*_{sens} are remarkably higher than those for the other rare gases, and the ionization of N₂O 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 N₂O⁺ is necessary for the formation of NO. The results obtained here can not be accounted for by the often-assumed mechanism²⁾;



because, according to this mechanism, more than one molecule of N₂ should be produced per electron. In order to explain the observed fact that one electron produces one or less molecule of N₂, one must assume the long-lived N₂O⁻ suggested by Freeman.³⁾ Recently Warman⁴⁾ has also obtained evidence for the initial formation of N₂O⁻ upon electron capture by N₂O. Thus, the major reaction may be tentatively described as follows:



followed by the combination of O and N to form O₂ and NO through NO₂. For the final conclusion to be attained, however, more supporting evidences are required.

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

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

4) J. M. Warman, private communication.

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