BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 2766—2771 (1970)

Ionic Processes in the Radiolysis of Nitrous Oxide. The Effect of Electron Scavenger and Rare Gas Sensitization

Satoshi TAKAO and Shoji SHIDA

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

(Received April 28, 1970)

The effect of electron scavenger (SF_6) on the radiolysis products of N_2O was examined. The sensitization of N_2O by various rare gases was also measured. In the presence of an electron scavenger we got 3.0 for the value of $-\Delta G(-N_2O)$ in good agreement with the value of $G(e^-)$ for N_2O. In the experiments of Xe or Kr containing small amounts of N_2O, the $G(-N_2O)$ values were nearly equal to the respective $G(e^-)$ values for the rare gases, and the addition of SF_6 to the Xe-N_2O system almost completely inhibited nitrogen formation. The results show that one electron decomposes just one molecule of N_2O. This fact can not be accounted for by the hitherto assumed mechanism, and a new mechanism involving N_2O^- is proposed for ionic processes in the radiolysis of N_2O. In the N_2O-rare gas mixtures of various compositions, the sensitized yields of N_2O decomposition per 100 eV energy absorbed by rare gases were divided into two groups, *e.g.*, the yields from He, Ne mixtures were about twice as large as those from Ar, Kr and Xe mixtures. This result is discussed in terms of charge transfer and the Penning ionization.

Nitrous oxide has been currently used as an effective electron scavenger in the study of liquid[1] and gaseous[2] hydrocarbon radiolysis. In these systems, the nitrogen yields which are considerably in excess of the estimated yields of electrons have been found, and many discussions are raised on the mechanism of the radiolytic formation of nitrogen from nitrous oxide in hydrocarbons.[3]

The study of the radiolysis of nitrous oxide in the gas phase has long received considerable attention in relation to the gas dosimeter, and a number of determinations of the radiolysis products have been reported,[4] but nothing definite has yet been established about the reaction mechanism.

The present study was undertaken in order to obtain a better insight of the mechanism for ionic processes in the radiolysis of N_2O by using SF_6 as an electron scavenger and various rare gases, especially Xe, as electron supplier.

Experimental

Nitrous oxide from a cylinder supplied by the Takachiho-Shoji Co. was freed from nitrogen and oxygen by careful degassing.

The gases SF_6 and CO_2 were used after the usual degassing. The rare gases were of high purity and used as obtained, the stated purities being 99.99%, 99.99%, 99.999%, 99.9% and 99.9% for He, Ne, Ar,

1) S. Sato, R. Yugeta, K. Shinsaka and T. Terao, This Bulletin, **39**, 156 (1966); N. H. Sagert and A. S. Blair, *Can. J. Chem.*, **45**, 1351 (1967).

2) for example, N. H. Sagert, R. W. Robinson and A. S. Blair, *Can. J. Chem.*, **46**, 3511 (1968).

3) for example, J. M. Warman, *J. Phys. Chem.*, **71**, 4066 (1967).

4) for example, J. A. Hearne and R. W. Hummel, *Radiat. Res.*, **15**, 254 (1961); G. R. A. Johnson, *J. Inorg. Nucl. Chem.*, **24**, 461 (1962); F. T. Jones and T. J. Sworski, *J. Phys. Chem.*, **70**, 1546 (1966).

Kr and Xe, respectively.

Irradiations were done in a cylindrical vessel of about 50 cc with ^{60}Co γ-rays at 25°C at a dose rate of 3.0×10^{19} eV/g/hr and the highest dose used was 7.2×10^{20} eV/g.

The initial products of radiolysis of nitrous oxide are N_2, O_2 and NO, but NO and O_2 were known to react to form NO_2 in a cold trap[5] and so the products, N_2 and O_2, after the cold trap reaction were measured by gas chromatography (a 5 m column of Molecular Sieve-5 A at room temperature). The initial amounts of NO formed were calculated stoichiometrically from the measured amounts of N_2 and O_2 and the initial amount of nitrous oxide.

The total energy absorbed in pure N_2O or mixtures was measured by the Fricke dosimeter making appropriate corrections for electron density. In the calculation of the total energy absorbed in these systems and the energy partition in mixtures, especially in the rare gas sensitization experiments, it would be better to use the relative stopping powers and the so-called effective atomic numbers suggested by Klots.[6] The results brought about slightly larger G-values (about 15% for all G_{sens}-values described below), but this does not change our conclusion. We advance discussions using the G-values obtained by the usual electron density corrections.

Results

The initial products, N_2, O_2 and NO from pure nitrous oxide of 50 to 400 mmHg pressures at room temperature have been determined. The observed G-values at 200 mmHg were $G(N_2)=10.1$, $G(O_2)=3.8$ and $G(NO)=5.1$ which were almost independent of pressure within experimental error. From these values we get 12.6 for the value of $G(-N_2O)$ in good agreement with those of Sworski[4] and other earlier investigators.

Although nitrous oxide is known to be an effective electron scavenger, SF_6 is much more effective in the gas phase,[7] and we could estimate the role of electrons in the radiolysis of N_2O by the addition of SF_6 to N_2O. The effect of adding SF_6 to N_2O of a constant pressure of 200 mmHg is shown in Fig. 1. The addition of very small amounts of SF_6 rapidly reduced the yields of N_2, O_2 and NO, which then remained constant on further addition of SF_6. The observed decreases were $-\Delta G(N_2)=2.1$, $-\Delta G(O_2)=0.6$ and $-\Delta G(NO)=1.8$, and thus the value of $-\Delta G(-N_2O)$ is calculated to be 3.0.

In Fig. 2 are shown the results with CO_2[8] which

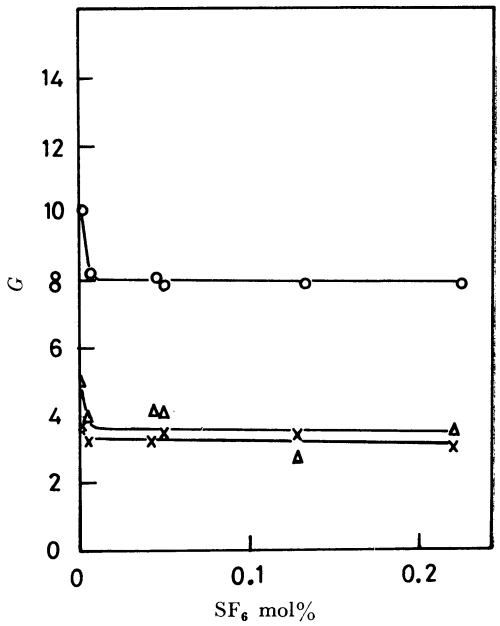

Fig. 1. The effect of adding SF_6 to N_2O on the yields of the products: ○, N_2; ×, O_2; △, NO.

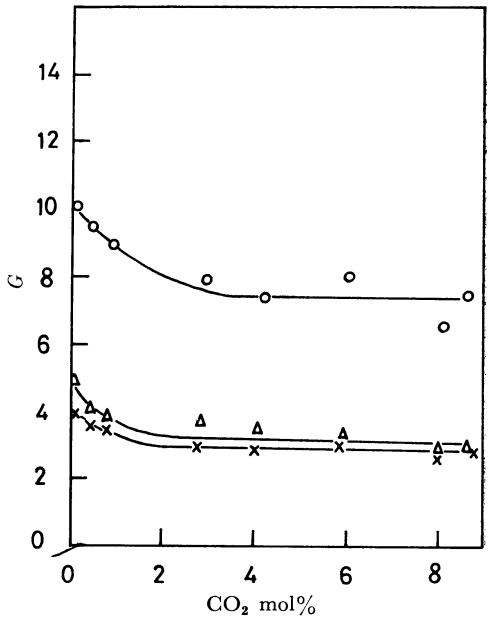

Fig. 2. The effect of adding CO_2 to N_2O: ○, N_2; ×, O_2; △, NO.

are similar to the above except for much slower levelling off of the G-values.

Figures 3 and 4 show, respectively, the results of the addition of N_2O to Xe and Kr of a constant pressure of 600 mmHg. All these values are corrected for the products formed by the direct radiolysis of N_2O.

Next, the effect of adding SF_6 to Xe including 5 mol% of N_2O was examined. Addition of

5) P. Burtt and J. F. Kircher, *Radiat. Res.*, **9**, 1 (1958).
6) C. E. Klots, *J. Chem. Phys.*, **46**, 3468 (1967).
7) G. R. A. Johnson and J. M. Warman, *Trans. Faraday Soc.*, **61**, 1709 (1965).
8) There are few reports in which CO_2 is used as an electron scavenger in the gas phase and no evidence in the electron attachment experiments that CO_2 is an electron scavenger (L. C. Christophorou and J. A. D. Stockdale, *J. Chem. Phys.*, **48**, 1956 (1968)). The results in Fig. 2 show nearly the same G-values as those in Fig. 1. In the present system, CO_2 may act as an electron scavenger.

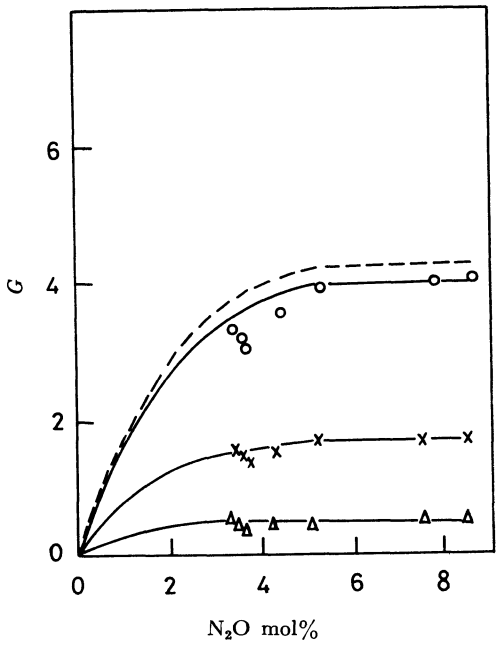

Fig. 3. The effect of adding N_2O to Xe: ○, N_2; ×, O_2; △, NO; ----, yields for $-N_2O$. In this figure and Fig. 4, corrections were made for the products arising from the direct radiolysis of N_2O.

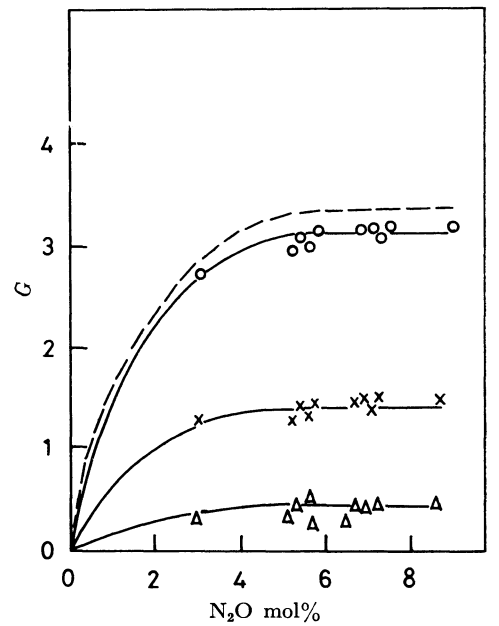

Fig. 4. The effect of adding N_2O to Kr: ○, N_2; ×, O_2; △, NO; ----, yields for $-N_2O$.

SF_6 of only 0.1% with respect to Xe completely inhibits nitrogen formation, indicating the electrons to be the primary precursor of products (Fig. 5).

We further studied the radiolysis of N_2O with

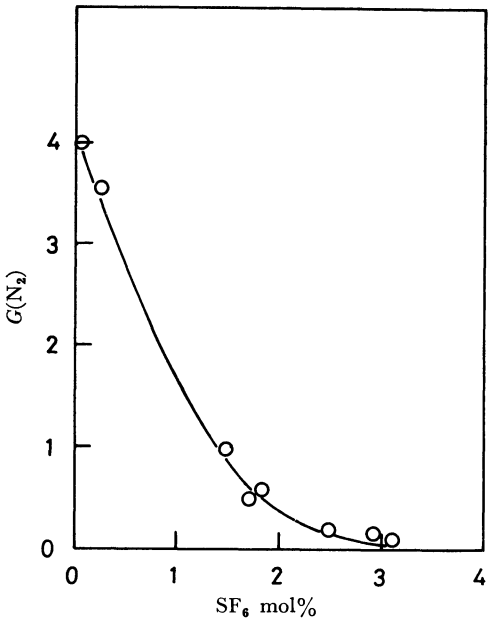

Fig. 5. The effect of adding SF_6 to Xe including 5 mol.% of N_2O. In this figure, SF_6 mol% shows the value with respect to N_2O.

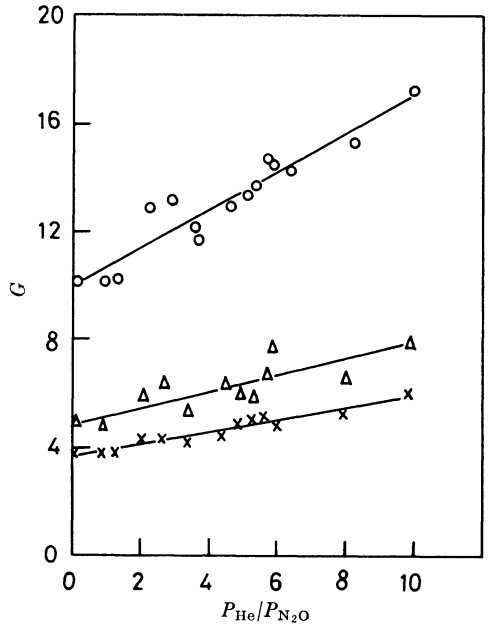

Fig. 6. Sensitization by He: ○, N_2; ×, O_2; △, NO. $P_{N_2O}=50$ mmHg.

various rare gases including those of higher ionization energies and metastable excitation energies. In Figs. 6—10, the results are shown with various ratios of rare gas to N_2O; the G-values are expressed as the number of molecules of products formed per 100 eV absorbed directly by N_2O. The amounts of N_2, O_2 and NO all increased linearly in the system of He and Ne, while in the

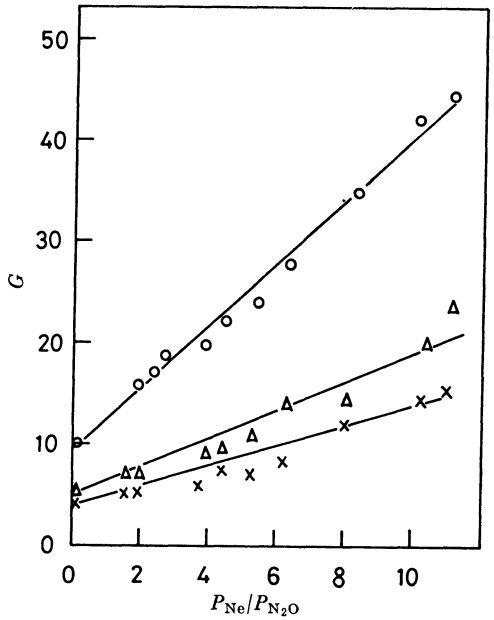

Fig. 7. Sensitization by Ne: ○, N_2; ×, O_2; △, NO. P_{N_2O} = 50 mmHg.

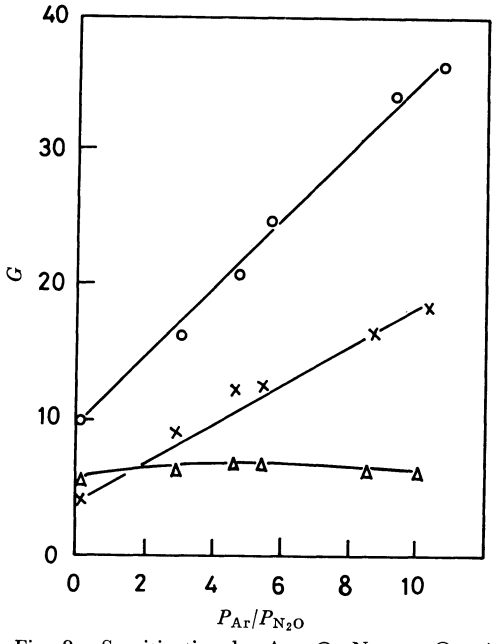

Fig. 8. Sensitization by Ar: ○, N_2; ×, O_2; △, NO. P_{N_2O} = 50 mmHg.

system of Ar, Kr and Xe, N_2 and O_2 increased linearly but the amounts of NO did not increase at all.

In order to investigate the effects of rare gas sensitization more quantitatively, we calculate the value represented as G_{sens}, that is, the increase in the G-value of a product by sensitization based on the energy absorbed by the rare gas as defined by the equation

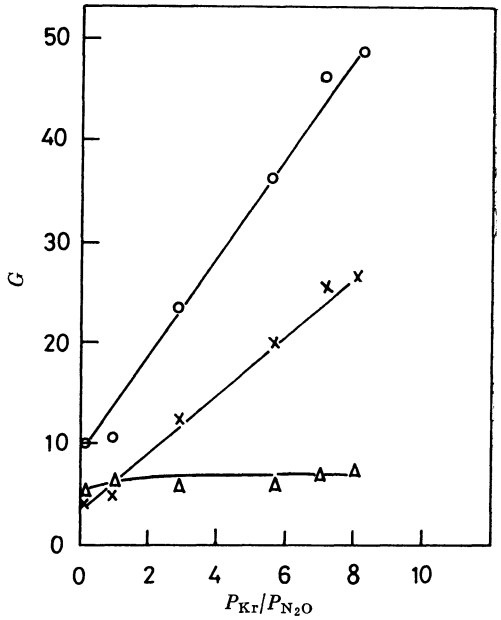

Fig. 9. Sensitization by Kr: ○, N_2; ×, O_2; △, NO. P_{N_2O} = 50 mmHg.

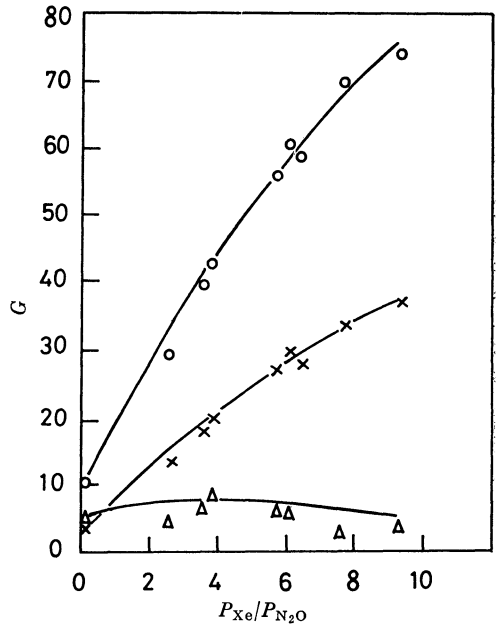

Fig. 10. Sensitization by Xe: ○, N_2; ×, O_2; △, NO. P_{N_2O} = 50 mmHg.

$$G_{sens} = (G_N R_N - G^\circ_N R_N)/R_r$$

where G°_N and G_N represent the values of the particular product based on the energy absorbed by N_2O in the N_2O pure system and in the sensitization experiment, respectively, and R_N and R_r the energy absorbed by N_2O and rare gas, respectively. The values obtained from the above equation are shown in Table 1.[9]

TABLE 1. G_{sens} VALUES FOR VARIOUS RARE GASES (The W-values and $G(e^-)$ values are also presented.)

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
$-N_2O$	8.8	7.9	3.0	3.2	4.1
W(eV)	42	37	26	24	22
$G(e^-)$	2.5	2.8	3.9	4.1	4.4

Discussion

From the experiments shown in Fig. 1, we get 3.0 for the value of $-\Delta G(-N_2O)$. This is in good agreement with the value of $G(e^-)=3.0$ calculated from $W(N_2O)=33$ eV.[10] If we assume that all electrons are scavenged by SF_6 and that the resulting SF_6^- does not contribute in any way to the decomposition of N_2O, it seems that one electron produced by the ionization of N_2O decomposes just one molecule of N_2O. If this is correct, the addition of small amounts of N_2O to Xe may result in the decomposition of N_2O close to the value of $G(e^-)$ expected from the W-value of Xe. This is the case for Xe and approximately for Kr (Figs. 3 and 4).

It is noted here that Xe has lower ionization energy than N_2O, while Kr has a higher one. However, experimental results showed that there was no appreciable difference between the Xe and the Kr systems and the product distributions were nearly the same in both cases. Thus in spite of the higher ionization potential of Kr, the charge transfer from Kr^+ to N_2O does not seem to occur effectively.

In the Xe-N_2O system as well as in other rare gas-N_2O systems, there is the possibility of excitation energy transfer from rare gas to N_2O besides that from the ionic processes:

$$Xe^* + N_2O \rightarrow N_2O^* + Xe$$

$$N_2O^* \rightarrow N_2 \text{ or other products}$$

Many photolysis data of nitrous oxide (λ: 1470, 1830 or 1849 A)[11-13] show that the ratio of NO to O_2 is greater than unity, but in the present Xe-N_2O system the ratio of NO to O_2 is less than 0.3. In the Xe-N_2O-SF_6 system, the formation of nitrogen was almost completely inhibited by SF_6, and we consider that there is no appreciable contribution from the excitation transfer processes.

Quite recently after the present work had been completed, Sears[14] reported the effect of addition of a small amount of SF_6 on the radiolysis of N_2O. His results and conclusion are not inconsistent with ours. Hummel[15] also reported experiments to determine the effect of small amounts of SF_6 on $G(N_2)$ at temperatures from 30 to 200°C. His results, however, were different from ours. We thought this discrepancy might lie mainly in the experimental conditions (he used a very large vessel of 1.9 l). Therefore we also examined the same system by using a larger vessel of about 400 cc, but the results obtained did not differ much from our earlier results obtained with a small vessel.

Thus we conclude that one electron decomposes one molecule of N_2O and yields one or less molecule of N_2 (0.7 and 0.9 molecules in pure N_2O and in Xe, respectively).

The results obtained here for ionic processes can not be accounted for by the hitherto assumed mechanism:[16]

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

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

According to this mechanism, more than one molecule of N_2 should be produced per electron, instead of the observed values of 0.7 and 0.9.

In order to explain the observed facts, we assumed a long-lived N_2O^- molecule resulting from the electron capture by N_2O, and proposed the following mechanism for the ionic processes in the radiolysis of pure N_2O.[17]

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

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

Consideration of the possible reaction schemes and reaction rate constants[18] led us to the assumption that the resulting O and N atoms react to form O_2 and NO through NO_2. Of course, the presence of other positive ions (NO^+, N^+, *etc.*) other than N_2O^+ could be considered as possible participants. There is the possibility that the difference of positive ions changes the decomposition mode and product formation. However, from the mass spectra of N_2O[19] it can be seen that only 36% of the parent ions decomposes. A number of studies have been reported of the mass spectra of N_2O, but ion-molecule reactions

9) Ausloos *et al.* (R. Gordon and P. Ausloos, *J. Res. Natl. Bur. Std.*, **69A**, 79 (1965)) studied the rare gas sensitization of $^{15}N^{14}NO$ by Kr and Xe and reported rather qualitative ion pair yields for nitrogen. Their results were consistent with ours qualitatively but not quantitatively. Their ion pair yields are approximate calculated values.

10) G. G. Meisels, *J. Chem. Phys.*, **41**, 51 (1964).

11) J. P. Doering and B.H. Mahan, *ibid.*, **36**, 1682 (1962).

12) N. R. Greiner, *ibid.*, **47**, 4373 (1967).

13) J. Y. Yang and F. M. Servedio, *ibid.*, **47**, 4817 (1967).

14) J. T. Sears, *J. Phys. Chem.*, **73**, 1143 (1969).

15) R. W. Hummel, *Chem. Commun.*, **1969**, 995.

16) for example, J. M. Warman, *Nature*, **213**, 381 (1967).

17) S. Takao, S. Shida, Y. Hatano and H. Yamazaki, This Bulletin, **41**, 2221 (1968).

18) G. B. Kistiakowsky and G. G. Volpi, *J. Chem. Phys.*, **27**, 1141 (1957).

19) R. C. Taylor, R. A. Brown, W. B. Young and C. E. Headington, *Anal. Chem.*, **20**, 396 (1948).

between positive fragment ions from N_2O^+ and N_2O molecules and their rate constants are not known in detail.[20] Charge transfer reaction is a likely one among many possible reactions. We assume then that some of these ions transfer their positive charge to N_2O to produce N_2O^+, eventually resulting in the neutralization of N_2O^+ with N_2O^-.

Recently, Warman and Fessenden[21] and Phelps and Voshall[22] reported the experimental facts showing that the electron capture of N_2O proceeds by a three-body process and suggested that N_2O^- ion is initially formed. Their results are consistent with our ionic processes in the radiolysis of N_2O.

In Table 1, we can classify the rare gases into two groups, *viz.*, He, Ne group and Ar, Kr, Xe group. The He, Ne group has much higher $G_{sens}(-N_2O)$ values than the Ar, Kr, Xe group. In the case of He and Ne the product distributions were nearly the same as in the direct radiolysis of N_2O, but in the case of Ar, Kr and Xe the yields of oxygen amount to about one-half of the nitrogen yields, NO being a minor product.

As mentioned before, the energy transfer from excited rare gas atom (X*) or ion (X^+) to N_2O molecule and the resulting decomposition of N_2O is possible in the rare gas sensitization such as

$$X^* \text{ or } X^+ + N_2O \rightarrow N_2 \text{ or other products.}$$

In the experiments with Ar, Kr and Xe, however, the $G_{sens}(-N_2O)$ values are nearly equal to the values of $G(e^-)$, and we believe that the energy transfer (charge or excitation) from Ar or Kr to N_2O does not occur in spite of the higher ionization potentials of Ar and Kr.

In the experiments with He and Ne, we observed nearly the same product distributions as in the direct radiolysis of N_2O and large $G_{sens}(-N_2O)$ values. We think that N_2O^+ ion produced by charge transfer in these systems could have considerable energy in excess of the ionization energy and that this might cause NO formation and large $G_{sens}(-N_2O)$ values in the rare gas sensitization by He and Ne. Of course, there is no saying that the difference in the object of neutralization of N_2O^- plays some part in the overall decomposition mechanism. In the case of He and Ne, the neutralization occurs between N_2O^+ resulting from charge transfer from He^+ or Ne^+ and N_2O^-, while in the case of Ar, Kr and Xe, the neutralization occurs between Ar^+, Kr^+ or Xe^+ and N_2O^-.

In the case of He and Ne, we must further take into account the formation of products from excitation energy transfer processes besides those from electron capture by N_2O and charge transfer to N_2O. We mentioned above that the results shown in Table 1 can be classified into two groups. From the discontinuity lying between Ne and Ar with respect to the product distributions and $G_{sens}(-N_2O)$ values, we remarked that the ionization potential of N_2O lies between the metastable energies of Ne and Ar. These conditions are shown in Table 2. It seems true that the product formation initiated from the Penning ionization of N_2O by metastable He or Ne atoms takes considerable part in the sensitization experiments with He and Ne, though we can not say to what extent.

Table 2. Ionization potentials and metastable excitation energies of rare gases[a]

	I.P. (eV)	E_m* (eV)
He	24.6	19.8
Ne	21.7	16.1
Ar	15.9	11.6
Kr	14.5	9.9
Xe	12.1	8.8
N_2O	12.9	—

a) G. R. A. Johnson and G. Scholes, "The Chemistry of Ionization and Excitation," Taylor and Francis Ltd., London (1967), p. 145.

The total processes in the rare gas sensitization are described as follows.

$$X \rightsquigarrow X^+ + e^- \quad (1)$$

$$\rightsquigarrow X_m^* \quad (2)$$

$$X^+ + N_2O \rightarrow N_2O^+ + X \quad (3)$$

$$X_m^* + N_2O \rightarrow N_2O^+ + X + e^- \quad (4)$$

$$e^- + N_2O \rightarrow N_2O^- \quad (5)$$

$$N_2O^- + N_2O^+ \rightarrow N_2 \text{ and other products} \quad (6)$$

$$N_2O^- + X^+ \rightarrow N_2 \text{ and other products} \quad (7)$$

where X_m* represents the metastable rare gas atom. Reactions (3), (4) and (6) do not occur in the case of Ar, Kr and Xe. Reaction (7) does not occur in the case of He and Ne. For overall radiolytic decomposition of N_2O in rare gases, the contribution from the neutral excited molecule decomposition by excitation transfer must be added except for the case of Ar, Kr and Xe. In the latter case, neither the excitation transfer from rare gas to N_2O nor the charge transfer takes place.

The authors wish to thank Dr. Y. Hatano and Dr. H. Yamazaki for many valuable suggestions throughout the course of this work. The authors gratefully acknowledge discussions with Professor G. R. Freeman, University of Alberta.

20) G. R. A. Derwish, A. Galli, A. Giardini-Guidoni and G. G. Volpi, *J. Chem. Phys.*, **40**, 3450 (1964).
21) J. M. Warman and R. W. Fessenden, *ibid.*, **49**, 4718 (1968).
22) A. V. Phelps and R. E. Voshall, *ibid.*, **49**, 3246 (1968).