

Radiolysis of $N^{15}N^{14}O^*$

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The gas-phase gamma-ray radiolysis of $N^{15}N^{14}O$ has been investigated as a function of dose, concentration, and temperature (-80 to 376 °C). Around 40 °C the ratios N_2^{30}/N_2^{29} and $N^{15}O/N^{14}O$ are 0.1 and 0.4, respectively, independent of dose and concentration. In the radiolysis of $N^{14}N^{14}O-N^{15}O$ mixtures it was found that the ion pair yield of N^{14} was 0.5. The ion pair yield of N_2^{29} in the radiolysis of $N^{15}N^{14}O$ increases with temperature from 2.6 at 50 °C to 21.7 at 376 °C. On the other hand, the yield of N_2^{30} is, within experimental error, not affected by a change in temperature, indicating that only the "molecular" nitrogen increases with an increase in temperature. The occurrence of dissociative electron attachment processes is consistent with the experimental observations. The yields of N_2^{29} and N_2^{30} increase when a potential difference is applied during radiolysis at the saturation plateau. The latter increase can be accounted for by an enhancement of neutral excited molecule decompositions. Addition of xenon and krypton enhances the decomposition of nitrous oxide. The results indicate that N atoms play a relatively less important role in the inert gas-induced decomposition than in the direct radiolysis.

1. Introduction

The radiolytic decomposition of nitrous oxide has been investigated on several occasions¹ using alpha-particles,^{2,3,4} accelerated electrons,⁵ X-rays^{6,7} or gamma rays.^{8,9}

At pressures around 1 atmosphere the number of N_2O molecules which undergo decomposition per ion pair is rather high (~ 4) and has been shown to increase as a result of (a) the effect of an applied field,^{3,4,6} (b) a decrease in pressure from 200 mm to 50^6 mm and (c) an increase in temperature¹ from 18 to 220 °C.

As a result of some of these observations, it has been suggested^{3,4,6} that neutral excited molecule decomposition may play an important role in the radiolysis of N_2O .

The present study was undertaken with the expectation that, by irradiating $N^{15}N^{14}O$, it might be possible to obtain a better insight of the radiolysis mechanism. Although not all of the results presented in this communication can be interpreted as yet, they are considered to be of sufficient interest to be reported, especially if one considers that N_2O has occasionally been proposed as a suitable gas-phase dosimeter.^{8,9}

2. Experimental Procedure

2.1. Materials

$N^{15}H_4N^{14}O_3$ was obtained from Isomet Corporation and had a stated purity of 95.3 percent N^{15} as labeled. Nitrous oxide was obtained by heating the ammonium nitrate until decomposition occurred. Purification was effected by thorough repeated outgassing at -195 °C followed by distillation from -130 to -195 °C.

The mass spectrum (Consolidated 21-101, 70 eV), given below,

14	6.56	31	2.59
15	5.68	32	0.07
16	4.71	44	5.42
28	0.70	45	100.
29	10.4	46	0.42
30	30.4	47	.2

indicates that the labeled nitrous oxide contained approximately 5.4 percent $N^{14}N^{14}O$ and 0.4 percent $N^{15}N^{15}O$. The cracking pattern indicates that at least 93 percent of the $N_2^{14,15}O$ consisted of $N^{15}N^{14}O$.¹⁰

$N_2^{28}O$ was obtained from Matheson Company, Incorporated and treated in exactly the same way as $N^{15}N^{14}O$.

$N^{15}O$ from Isomet contained 2.5 percent $N^{14}O$. Chemical impurities were removed by outgassing the nitric oxide at -210 °C followed by distillation from a low temperature distillation column maintained at -185 °C. $N^{14}O$ obtained from Matheson Company, Incorporated was treated in a similar fashion.

¹⁰ This estimate is based on the ratio of mass 31 to mass 30 as an upper limit of the impurity, because mass 31 can also be produced by a decomposition of $N^{15}N^{14}O^+$. The fact that the ratio $N_2^{15,15}O/N_2^{14,15}O$ is not much higher than expected from the natural abundance of N^{15} , also suggests that labeling of the center nitrogen atom of nitrous oxide is negligible.

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¹ For a review see: S. C. Lind, Radiation Chemistry of Gases (Reinhold Publishing Corp., New York, 1961), p. 243.

² E. Wourtsel, Le Radium **11**, 342 (1919); J. Phys. Radium **1**, 77 (1920).

³ H. Essex and A. D. Koluban, J. Chem. Phys. **8**, 450 (1940).

⁴ H. Essex and N. T. Williams, J. Chem. Phys. **16**, 1153 (1948).

⁵ G. Gedye, J. Chem. Soc., 3016 (1931).

⁶ B. P. Burt and J. F. Kircher, Rad. Res. **9**, 1 (1958).

⁷ G. R. A. Johnson, Proc. Chem. Soc., p. 213, June 1960.

⁸ P. Hardeck and S. Dondes, Nuclonics **14**, 66 (1956).

⁹ R. W. Hummel and J. A. Hearne, Nature **188**, 734 (1960).

3. Results

Labeled oxygen obtained from Isomet was as stated, 95.2 percent O_2^{18} .

Phillips research grade ethylene was degassed at $-195^\circ C$.

Krypton and Xenon were assayed reagents from Airco.

2.2. Irradiation Procedure

The geometry of the gamma-ray sources was identical to that previously described.¹¹ The source used in this work had an intensity of $3000 \text{ esu/cm}^3/\text{sec}$ in December of 1961.

Most radiolysis experiments were carried out in 300 cm^3 Pyrex vessels, which were equipped with a break seal and were heated close to the melting point of Pyrex prior to being filled. The vessels could be heated during radiolysis by a cylindrical furnace controlled by a Variac. In one experiment, capillary tubing (3 mm i.d.) attached to a break seal was used to contain the solid nitrous oxide which was irradiated at $-195^\circ C$.

Accurate values of the ion pair yields were based on the measurement of the ion current in the saturation region. For this purpose, a cylindrical cell (500 cm^3 volume) was constructed with an outer steel wall (6.65 cm i.d.) as the anode, and a centrally located inner electrode (1.62 cm o.d.) as the cathode. The two electrodes were joined through glass to metal seals and a grounded guard ring. The dead space required a 4 percent correction. Taking a value of 30 eV for W , the energy absorbed by nitrous oxide was $60 \times 10^{17} \text{ eV M}^{-1} \text{ sec}^{-1}$ in the stainless steel vessel. Additional applied field experiments were carried out in a 200 cm^3 graphite coated Pyrex cell which was similar in design to that used by Back et al.¹²

The light source for a few $Hg(^3P_1)$ sensitized experiments, which were carried out in connection with this study, was a flat-spiral, low pressure mercury arc obtained from Hanovia. A Corning 7-54 filter was used to eliminate wavelengths below 2200 \AA .

2.3. Analysis

The products analyzed were nitrogen, oxygen, and nitric oxide. Nitrogen and oxygen were distilled from a trap at $-210^\circ C$ by means of a Toepler pump. Nitric oxide was removed from a modified Ward still held at $-185^\circ C$. After measurement in a gas burette, they were further analyzed in a Consolidated 21-101 mass spectrometer.

No attempt was made to determine the yield of NO_2 . Also, it was assumed that some portion of the NO_2 was converted to nitric oxide through reaction with mercury in the analysis system, thus contributing to the yield of the latter product.

The results reported in tables 1, 2, and 3 have been expressed in rates per mole of nitrous oxide, rather than in ion pair yields, because the experiments were carried out in ordinary Pyrex vessels in which the saturation current could not be measured. Because all experiments were carried out at the same dose rate, approximate ion pair yields in the pure nitrous oxide experiments can be estimated by dividing the rates by the constant factor 2.01×10^{17} . This factor is based on the assumption that the ion pair yield of nitrogen is the same in the stainless steel vessel used for the dosimetry experiments as in the Pyrex vessel under otherwise identical experimental conditions. The ion pair yields (M/N) of N_2^{29} given in table 3 are only approximate calculated values based on the W -values¹ of Xe and Kr. In addition to the results given in the tables, the following information should be reported:

3.1. $Hg(^3P_1)$ Sensitized Photolysis

A few $Hg(^3P_1)$ sensitized experiments were carried out at a concentration of $N^{15}N^{14}O$ of $1.8 \times 10^{-6} \text{ mole/cm}^3$ from 30 to $250^\circ C$. The isotopic distribution of the product nitrogen agrees within experimental error with what is to be expected considering the mass spectrum of the $N^{15}N^{14}O$ used in this investigation (i.e., 5.4:100:0.4 for N_2^{28} , N_2^{29} , and N_2^{30} respectively).

In these experiments, the yield of oxygen is within 5 percent one-half the total nitrogen at all temperatures. NO is a very minor product. Even at $250^\circ C$, the yield of nitric oxide is only about 2 percent of the nitrogen. The formation of oxygen is completely quenched by 2.6 percent of ethylene.

3.2. Radiolysis—Effect of Dose

It should be noted that in the tables " $N_2^{30} \text{ corr}$ " is equal to the measured yield of N_2^{30} minus $0.004 \times N_2^{29}$. The latter term essentially represents the N_2^{30} formed by elimination from the 0.4 percent $N_2^{30}O$ present in the nitrous oxide.

At $30^\circ C$, the ion pair yield of N_2^{28} produced in the radiolysis of $N_2^{28}O$ at 5 and 14.9 cm pressure was 3.37 and 3.21 respectively. The conversion in these experiments as well as in all of those reported in the tables was 0.1 percent or less. These ion pair yield values are in rather poor agreement with the room temperature values of 4.74 and 3.72 reported by Burt and Kircher⁶ for pressures of 5 and 20 cm respectively, but are in good correspondence with the value of 3.36 ± 0.1 reported by Harteck and Dondes⁸ for an unspecified temperature. Experiments carried out with $N^{15}N^{14}O$ gave, within experimental error, the same ion pair yield for $N_2^{29} + N_2^{30} + N_2^{28}$ as is observed for N_2^{28} with $N_2^{28}O$. At $40^\circ C$ and a pressure of 5 cm in these experiments, a value of 0.10 is obtained for the ratio N_2^{30}/N_2^{29} and a value of 0.45 for the ratio $N^{15}O/N^{14}O$.

The values for these ratios are independent of conversion from 0.03 to 3 percent but show a slight

¹¹ P. Ausloos and R. Gorden, Jr., *J. Chem. Phys.* **36**, 5 (1962).

¹² R. A. Back, T. W. Woodward, and K. A. Laughlan, *Can. J. Chem.* **40**, 1380 (1962).

(5%) decrease with increase in pressure from 5 cm to 20 cm. After correcting for the N_2^{28} produced from the radiolysis of the 5.4 percent $N_2^{28}O$ in $N^{15}N^{14}O$, the value of the ratio N_2^{28}/N_2^{29} becomes approximately 0.04. At the low conversions used in this work, the latter value is however necessarily less accurate than the values of N_2^{30}/N_2^{29} which are not affected by the presence of traces of N_2^{28} which may be

released from the wall of the reaction vessel during irradiation or introduced in the system in the course of the analytical procedure.

The analysis of NO and O_2 is, in most cases, not quantitative for reasons enumerated by Burt and Kircher.⁶ However, secondary reactions of the type mentioned by these authors should not affect the isotopic distributions.

TABLE 1. Effect of nitric oxide and oxygen

Nitrous Oxide mole/cm ³ ×10 ⁶	Additive percent	Time minutes	Rates, molecules M ⁻¹ sec ⁻¹ ×10 ⁻¹⁷				N ₂ ³⁰ corr/N ₂ ²⁹
			N ₂ ²⁸	N ₂ ²⁹	N ₂ ³⁰	N ¹⁴ O	
N ¹⁴ N ¹⁴ O	N ¹⁵ O						
2.71		60	5.85			1.26	
2.68	0.25	6	6.13	0.92	0.232	4.42	
2.70	0.25	15	5.58	0.80	0.296	2.99	
2.67	5.7	60	4.9	1.06	0.207		
N ¹⁵ N ¹⁴ O	N ¹⁴ O						
2.73		15	0.5	5.35	0.56		0.100
2.74	1.6	15	0.72	5.2	0.46		0.085
2.70	7.9	60	1.0	5.1	0.35		0.065
2.75	26.0	60	1.3	5.15	0.305		0.055
N ¹⁵ N ¹⁴ O	O ₂ ¹⁸						
2.67	4.0	60	0.7	4.99	0.603		0.117

TABLE 2. Effect of temperature *

T °C	Rates, molecules M ⁻¹ sec ⁻¹ ×10 ⁻¹⁷						N ₂ ³⁰ corr/N ₂ ²⁹	N ¹⁵ O/N ¹⁴ O
	N ₂ ²⁸	N ₂ ²⁹	N ₂ ³⁰	O ₂	N ¹⁴ O	N ¹⁵ O		
-195 (solid)	0.6	9.72	0.148	2.6	0.53	0.34	0.011	0.64
-80		4.94	.482	.56	.81	.33	.094	.41
40	.5	5.35	.56	.67	1.11	.51	.10	.46
83	1.15	5.9	.64	<.01	2.2	1.2	.105	.54
150	1.61	13.6	.92		9.36	6.15	.064	.06
250	3.17	26.7	1.03		24.0	19.0	.034	.79
310	3.71	34.5	1.00		31.0	26.1	.025	.84
376	5.36	43.7	1.11		39.3	33.4	.021	.85
50 ^a		4.45	0.477				.103	
150 ^a		6.38	.582				.087	.54
275 ^a		14.7	.60				.037	
277 ^b		11.9	.457		3.91	2.65	.034	
165 ^c		3.73	.223	.219			.056	

* The concentration of N¹⁵N¹⁴O in all gas-phase experiments was 2.7×10⁻⁶ mole/cm³.

^a 2.3 percent ethylene was added.

^b 11.4 percent ethylene was added.

^c 40 percent I₂ added.

TABLE 3. Effect of inert gases

Inert/N ¹⁵ N ¹⁴ O	N ¹⁵ N ¹⁴ O mole/cm ³ ×10 ⁶	T °C	Rates, molecules M ⁻¹ sec ⁻¹ ×10 ⁻¹⁷						N ₂ ³⁰ corr/N ₂ ²⁹
			N ₂ ²⁸	N ₂ ²⁹	N ₂ ³⁰	O ₂	N ¹⁴ O	N ¹⁵ O	
Xenon/N ¹⁵ N ¹⁴ O:									
4.13	1.08	50	5.18	35.2 (2.4)	2.57	11.9	4.2	1.64	0.069
4.18	1.05	200	15.5	84.4 (5.65)	4.44	<1.0	66.3	47.8	.049
4.02 ^a	1.08	50	7.58	27.0 (1.9)	0.656	<1.0			.020
4.05 ^b	1.07	50	5.3	26.5 (1.85)	0.688	<1.0			.022
9.7	1.07	50	10.8	79.4 (2.45)	4.61	22.3			.054
Krypton/N ¹⁵ N ¹⁴ O:									
5.66	1.13	50	4.35	36.0 (2.65)	2.73	4.38			.072
12.3	1.07	50	8.3	66.6 (2.4)	4.84	11.2			.069

Values given in parentheses are M/N values.

^a 2.0 percent N¹⁴O added.

^b 6.9 percent N¹⁴O added.

3.3. Effect of Nitric Oxide and Oxygen

In table 1, it is seen that N_2^{29} is an important product in the radiolysis of $N^{15}O-N^{14}N^{14}O$ mixtures. An increase in the added percentage of $N^{15}O$ from 0.25 to 5.7 raises the yield of N_2^{29} only slightly. Addition of 0.25 percent $N^{15}O$ to $N^{14}N^{14}O$ also results in appreciable increase of the measured product, $N^{14}O$. This can be ascribed to the fact that, under these conditions, oxygen will mainly react with the added $N^{15}O$ to produce $N^{15}O_2$, instead of reacting with the product $N^{14}O$ which is present at a relatively smaller concentration. The decrease of $N^{14}O$ with increase in conversion (table 1) can thus be attributed to the increased probability for oxygen to react with $N^{14}O$. It can be noticed that N_2^{30} is a minor product in all $N_2^{14}O-N^{15}O$ experiments.

Addition of O_2^{18} to $N^{15}N^{14}O$ did not appreciably affect the rate of formation of N_2^{29} and N_2^{30} , but did lead to the production of appreciable yields of $N^{14}O^{18}$ and $N^{15}O^{18}$. A value of 0.44 was obtained for the ratio $(N^{15}O^{16} + N^{15}O^{18}) / (N^{14}O^{16} + N^{14}O^{18})$ which is comparable to the values for the ratio $N^{15}O/N^{14}O$ obtained in the radiolysis of $N^{15}N^{14}O$. These observations indicate that oxygen reacts with nitric oxide to form NO_2 of which a certain fraction is reconverted to NO prior to or during analysis. The latter reaction does apparently not affect the ratio $N^{15}O/N^{14}O$.

3.4. Effect of Temperature

Table 2 and figure 1 are mainly concerned with the effect of temperature at constant concentration of

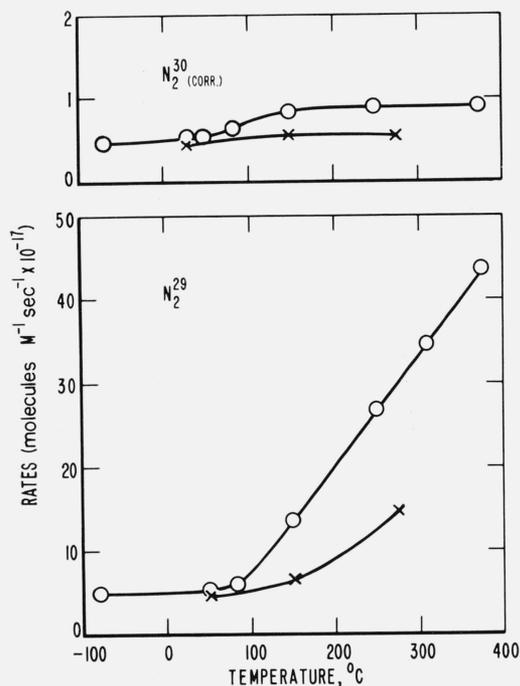


FIGURE 1. Effect of temperature on the γ -radiolysis of $N^{15}N^{14}O$.
X, 2.3% C_2H_4 added.

$N^{15}N^{14}O$. One solid phase experiment, carried out at $-195^\circ C$, has been included in the table. The most striking features of the solid phase radiolysis are (a) the low relative yield of N_2^{30} and (b) the high measured yield of O_2 .

In the gas phase at temperatures from -80° to 376° , there is a marked increase of N_2^{29} , $N^{14}O$, and $N^{15}O$, as well as of the product ratio $N^{15}O/N^{14}O$. On the other hand, the ratio N_2^{30}/N_2^{29} goes through a maximum and the yield of N_2^{30} increases only very slightly especially at the higher temperatures. It can be seen that the effect of temperature is much less pronounced when 2.3 percent C_2H_4 has been added to $N^{15}N^{14}O$. A further increase in the percentage of ethylene from 2.3 to 11.4 has only a minor effect on the product yields. The addition of iodine quenches the formation of nitrogen.

Blank experiments, carried out up to $400^\circ C$, under identical conditions to those in the experiments listed in table 2, except for the actual irradiation, did not show any detectable products.

3.5. Effect of Inert Gases

Several $N^{15}N^{14}O-Xe$ mixtures were irradiated and the results are given in table 3. Ion pair yields of N_2^{29} are given in parentheses. It can be noted that in the inert gas sensitized radiolysis, oxygen is a more important product than in the direct radiolysis, although the analytical procedure was the same in both cases. A rise in temperature from 50 to $200^\circ C$ shows qualitatively the same enhancing effect on the product yields as in the direct radiolysis.

3.6. Effect of Applied Field

In figure 2, the ion current and the ion pair yields

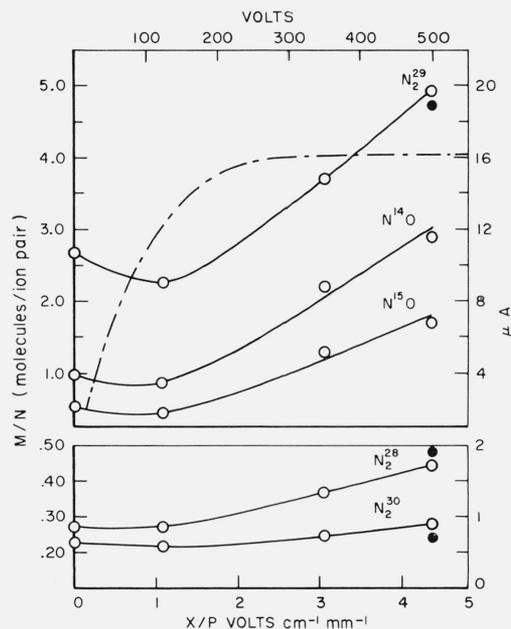
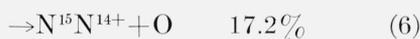
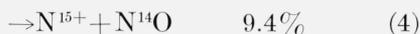
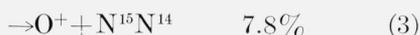
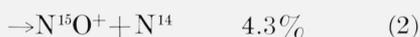


FIGURE 2. Effect of electric fields on the γ -radiolysis of $N^{15}N^{14}O$.
●, 2.5% C_2H_4 added. — — — ion current in μA .

of the products formed when an electrical field is applied during the radiolysis are given. These experiments were carried out in a graphite coated cell. It may be noted that in this reaction vessel, even in the absence of an applied field, the yields of $N^{15}O$ and $N^{14}O$ were larger than in an ordinary Pyrex vessel (table 2). Also, oxygen could not be detected as a product. It may thus be surmised that oxygen disappears on the wall of the reaction vessel. The addition of 2.5 percent ethylene to nitrous oxide at the highest field strength reduced the yield of N_2^{29} by only 4 percent.

4. Discussion

From the cracking pattern of $N^{15}N^{14}O$, it can be deduced that, at 70 eV, only about 35 percent of the parent ions decompose. The major modes of fragmentation of the positive parent ion at 70 eV are as follows:



Besides the formation of the positive ions dissociative electron attachment has to be considered^{13, 14} as well. In the case of $N^{15}N^{14}O$, the latter process can be represented thus:



In addition to the production of ions in the initial events the formation and decomposition of neutral excited molecules may also be of importance. It is obvious that on the basis of data reported in this paper, a detailed discussion of the different reaction mechanisms is unwarranted. An attempt will, however, be made to account for some of the processes which lead to the formation of N atoms and N_2 molecules.

4.1. Evaluation of G(N)

Although the results provide a rather accurate estimate of the relative yield of N_2^{30} produced in the radiolysis of $N^{15}N^{14}O$, one cannot immediately deduce a value of G(N^{15}). It is indeed known that ground state N atoms do not readily react with

nitrous oxide,¹⁵ but will undergo a fast reaction with the product nitric oxide to form a nitrogen molecule¹⁶



This is supported by the results given in table 1. For instance, the relatively large yield of N_2^{29} in the radiolysis of $N^{14}N^{14}O-N^{15}O$ mixtures, containing only 0.25 percent $N^{15}O$, clearly demonstrates the importance of reaction 8. From these results it would follow that about 20 percent of the total nitrogen is formed by this reaction. At 40 °C this would correspond to a value of M/N=0.5 in good agreement with an earlier estimate by Hardeck and Dondes.⁸

If N_2^{30} in the radiolysis of $N^{15}N^{14}O$ is entirely formed by the reaction



it may be expected that, at short conversions, small amounts of added $N^{14}O$ should prevent the formation of N_2^{30} in the radiolysis of $N^{15}N^{14}O$ by way of reaction 10.



Consequently, the fact that, in mixtures containing up to 26 percent $N^{14}O$, N_2^{30} is still an important product indicates that besides reaction 9, one or more as yet unidentified processes involving a nitrous oxide molecule must contribute to the formation of N_2^{30} . The presence of electronically excited N atoms, N^+ or N_2O^+ , may have to be considered as possible participants.

If we assume that all N atoms which are produced in the radiolysis of $N^{15}N^{14}O$ react with $N^{15}O$ and $N^{14}O$ at the same rate, then a value of 0.38 can be deduced for the ion pair yield of N^{15} after correcting the yield of N_2^{30} for the residual yield of N_2^{30} observed in the $N^{15}N^{14}O-N^{14}O$ experiments. Because the latter value is considerably larger than the ion pair yield of 0.18 estimated from the mass spectrum pattern, it may be concluded that other processes besides 1 must contribute to the formation of N^{15} atoms. As will be shown later, decomposition of neutral excited nitrous oxide formed by electron impact or by neutralization of the parent ion may be an additional source of N^{15} atoms. Recent photochemical studies by Doering and Mahan¹⁷ have indeed shown that the process



is of importance at wavelengths ranging from 1236 to 1830 Å.

¹⁵ G. B. Kistiakowski and G. G. Volpi, J. Chem. Phys. **27**, 1141 (1957).

¹⁶ (a) John T. Herron, J. Research NBS **65A**, 411 (1961). (b) R. A. Back and J. Y. Mui, J. Phys. Chem. **66**, 1362 (1962).

^{17a} J. P. Doering and B. H. Mahan, J. Chem. Phys. **34**, 1617 (1961).

^{17b} J. P. Doering and B. H. Mahan, Ibid **36**, 1682 (1962).

¹³ R. K. Curran and R. E. Fox, J. Chem. Phys. **34**, 1590 (1961).

¹⁴ G. J. Schulz, J. Chem. Phys. **34**, 1778 (1961).

4.2. Formation of "Molecular" Nitrogen

N_2^{29} can be eliminated as a molecule from $N^{15}N^{14}O$ in several different ways. Besides initial events such as neutral excited molecule decompositions¹⁷ or dissociative electron attachment,^{13, 14} secondary reactions such as^{18, 6}



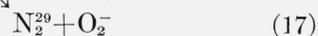
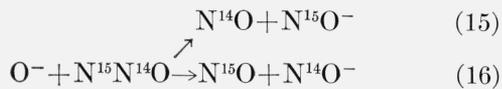
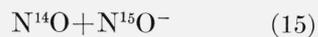
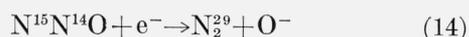
may also lead to the formation of this product.

The effect of temperature provides us with probably the most interesting information about at least one mode of formation of "molecular" nitrogen. It should first be noted that the observed increase in the yield of nitrogen from -80 to 376 °C (tables 2, 3, fig. 1) which cannot be due to the pyrolysis of nitrous oxide under our experimental conditions up to 400 °C (see Results) can also not be explained by an increase in neutral excited molecule decomposition for the following reasons:

(1) There is, within experimental error, no increase in the yield of " N_2^{30} corr" from 150 to 376 °C¹⁹ indicating the non-enhancement of process 11 which, as shown recently¹⁷ should occur when highly excited nitrous oxide molecules decompose independent of the degree of excitation.

(2) Lower excited nitrous oxide molecules such as those produced in the $Hg(^3P_1)$ sensitized decomposition do not eliminate an N atom but do produce an O atom in the 3P or 1D state which does not react any further with nitrous oxide even up to 250 °C (see Results). The results of table 2, however, show that the yield of nitric oxide increases as fast as that of N_2^{29} indicating that, if a neutral O atom is produced at high temperatures, it does react readily with nitrous oxide and so cannot be in the 3P or 1D state.

By the process of elimination we suggest the occurrence of the negative ion reactions proposed before by other investigators^{3, 4, 6}



which, at elevated temperatures, must be followed by a reaction which regenerates O^- in order to account for the temperature effect. Processes such as 18 and 19 may be considered



¹⁸ M. Zelkoff and L. M. Aschenbrand, J. Chem. Phys. **22**, 1680 (1959).

¹⁹ The slight increase in " N_2^{30} corr" from 150 to 376 °C can be entirely accounted for by the increase of the ratio $N^{15}O/N^{14}O$ which enhances the reaction of N^{15} with $N^{15}O$.

Reaction 19 must be of less importance than reaction 18 because at the highest temperature the material balance N_2/NO approaches the value 0.5, indicating that O_2 can only be formed in small yields. The following observations favor the proposed negative ion chain reaction:

(1) An electron trap such as iodine effectively reduces the yield of N_2^{29} to a value which is lower than that obtained at -80 °C.

(2) As may be expected from the above mechanism, the effect of temperature is not related to the manner by which the secondary electrons are produced. This is demonstrated by the fact that an increase in temperature in the xenon-induced decomposition of $N^{15}N^{14}O$ affects the product yields in very much the same way as in the direct radiolysis although there are considerable differences in the initial radiolytic processes occurring in the two systems at 40 °C.

(3) Small amounts of ethylene suppress the yield of N_2^{29} . Such an effect would not be expected to occur if neutral excited molecules are involved. This has been corroborated by a few experiments carried out in our laboratory at 1236 Å, and by the negligible effect of ethylene in the applied field experiments (see Results). Ethylene may, however, be expected to intercept O^- or NO^- , thus reducing the yield of N_2^{29} .

(4) At the highest temperatures, $N^{15}O$ becomes equal to $N^{14}O$.

In view of the foregoing, it may be concluded that nitrous oxide can only be recommended as a dosimeter provided the temperature is carefully controlled. The absence of a temperature effect up to 200 °C, mentioned in an earlier study,⁸ is inconsistent with the present data.

In the solid phase radiolysis experiment the relatively low yield of N_2^{30} and the high yield of O_2 indicates that the dissociation of $N^{15}N^{14}O$ into N_2^{29} and $O(^3P)$ or $O(^1D)$ occurs with a relatively higher probability than in the gas phase.

4.3. Effect of Applied Field

The effects of applied field on the product yields from $N^{15}N^{14}O$ are very similar (fig. 2) to those reported by Burt and Kircher⁶ for $N_2^{28}O$.

As previously suggested,⁶ ion recombination can account for the initial decrease in the yields of nitrogen and nitric oxide with increasing X/P (field strength/unit pressure in mm). Woodward and Back²⁰ came to a similar conclusion regarding the decrease in the yield of hydrogen from hydrocarbons irradiated in the presence of increasing electric field.

As the field strength is increased in the region of current saturation there is a pronounced increase in the yield of nitric oxide, N_2^{29} , and to a lesser degree N_2^{30} without an accompanying increase in the ion pair production. The negligible effect of ethylene (see Results) indicates that the increase of N_2^{29} cannot be accounted for by the same negative ion mechanism as has been proposed to account for the effect of temperature. Excitation of $N^{15}N^{14}O$ by the accelerated electrons followed by a reaction mechanism analogous to that observed in the vacuum

²⁰ T. W. Woodward and R. A. Back, Can. J. Chem. **41**, 1463 (1963).

u.v. photolysis¹⁷ is the most likely explanation for the observed increase in ion pair yields [3, 4, 6]. A similar effect of electrical fields is found to play an important role in the decomposition of hydrocarbons.²¹

4.4. Inert Gas Induced Decomposition of Nitrous Oxide

The Xe-N₂²⁹O experiments show (table 3) that energy is transferred efficiently from xenon to nitrous oxide although the appearance potential of N₂O⁺ (12.63 eV)¹⁴ is above that of the xenon ion in the ³P_{3/2} state which is considered to be the major ion produced by electron impact. The M/N values of N₂²⁹ are, however, somewhat lower than in the direct radiolysis.

The major differences between the product distributions in the xenon induced and direct radiolysis are: (a) the lower values of the ratio N₂³⁰/N₂²⁹, both in the presence and absence of N¹⁴O and (b) the higher yield of O₂. The first observation can readily be accounted for by the fact that the parent ion decomposition according to process 1 will be of less importance in the xenon induced decomposition. The higher yield of O₂ implies a low yield of NO and can tentatively be ascribed to the formation of O atoms in the low lying ¹D or ³P levels. Very similar conclusions can be drawn from the krypton experiments except that, as may be expected in this case, the relative yield of O₂ is lower than in the xenon induced decomposition. It may be noted that the dissociative process 1 accounted for only 11 percent of the total ionization²² in the charge transfer mass spectrum between Kr⁺ and N₂O.

²¹ P. Ausloos and R. Gorden, Jr., J. Chem. Phys. **41**[1278 (1964).

²² E. Lindholm, Z. Naturforsch. **9a**, 535 (1954).

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