

[Reprinted from the Journal of Physical Chemistry, **70**, 1546 (1966).]
Copyright 1966 by the American Chemical Society and reprinted by permission of the copyright owner.

Nitrous Oxide Dosimetry. Effects of Temperature, Pressure, and Electric Field¹

by F. T. Jones² and T. J. Sworski³

Union Carbide Corporation, Nuclear Division, Research Center, Tuxedo, New York (Received November 8, 1965)

The N₂O dosimeter was calibrated for 1-Mev electrons by ionization measurements. $G_{N_2} = 10.0 \pm 0.2$, $G_{O_2} = 4.0 \pm 0.4$, $G_{NO} = 3.9 \pm 0.3$, and $G_{-N_2O} = 12.0 \pm 0.4$ are initial yields at 24° and 600 torr. All yields increase with increasing temperature. The ratio G_{NO}/G_{O_2} increases from 1.0 at 24° and 600 torr to greater than 2.0 above 150°. Therefore, owing to reaction between NO and O₂, the volatile products after trapping at -196° consist of only N₂ and O₂ at 24° and only N₂ and NO above 150°. Although G_{-N_2O} and G_{N_2} are essentially independent of pressure from 50 to 600 torr, G_{O_2} decreases and G_{NO} increases with decreasing pressure. The G value for O₂ volatile after trapping at -196° decreases from 2.0 at 600 torr to 0.9 at 50 torr at 24°. Product yields are increased by electrical fields insufficient to induce secondary ionization but sufficient to induce electronic excitation. The pressure dependence for G_{N_2} and G_{NO} at $X/p \sim 11$ v cm⁻¹ torr⁻¹ is consistent either with ultimate dissociative electron capture of all electrons and bimolecular deactivation of N₂O* or with no significant electron capture and termolecular deactivation of N₂O* with $\tau_{N_2O^*} \sim 10^{-9}$ sec.

Introduction

A ferrous sulfate solution in air-saturated 0.4 *M* sulfuric acid is commonly used as a radiation dosimeter. Reported values for $G(Fe^{3+})$ of 15.6 ± 0.3^4 and 15.8 ± 0.3^5 for ⁶⁰Co γ radiation and 15.45 ± 0.11^6 for 2-Mev electrons indicate the excellent agreement achieved in calibrations of this dosimeter.

Harteck and Dondes⁷ proposed the use of N₂O for gas phase dosimetry. Energy absorption in gases can be determined by measurement of the rate of ionization during radiolysis. This technique, however, has produced a wide disparity in calibrations of the nitrous oxide dosimeter: $G(N_2) = 12.4 \pm 0.4$ for ⁶⁰Co γ -radiation⁸ and $G(N_2) = 11.3 \pm 0.4$ for 70-kvp X-rays,⁹ both calibrated by ionization measurements, are much larger than $G(N_2) = 10.3 \pm 0.3$ reported by Harteck and Dondes⁷ (all G values are recalculated on the basis of $W_{N_2O} = 32.9$).

Experimental techniques have been developed in our laboratory¹⁰ which enable dosimetry in the gas phase to be carried out by ionization measurements with a precision of better than $\pm 1\%$ with an electron accelerator. We, therefore, calibrated the nitrous oxide dosimeter and determined the effects of temperature, pressure, and electrical field.

Experimental Section

Materials. Nitrous oxide (Matheson Co.) was introduced into the vacuum system through a column of KOH pellets and followed by repeated degassing of the condensed solid at 77°K and subsequent distilling at 193°K until N₂, O₂, NO, and NO₂ could not be detected by the analytical methods used for these products of irradiation.

Analysis. Products not condensable at 77°K were analyzed by either combustion analysis or mass spectrometry. Combustion analysis was employed for samples containing only N₂ and O₂. Hydrogen, puri-

(1) Presented at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

(2) Department of Chemistry, Stevens Institute of Technology, Hoboken, N. J.

(3) Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn.

(4) C. J. Hochanadel and J. A. Ghormley, *J. Chem. Phys.*, **21**, 880 (1953).

(5) R. M. Lazo, H. A. Dewhurst, and M. Burton, *ibid.*, **22**, 1370 (1954).

(6) R. H. Schuler and A. O. Allen, *ibid.*, **24**, 56 (1956).

(7) P. Harteck and S. Dondes, *Nucleonics*, **14**, No. 3, 66 (1956).

(8) G. R. A. Johnson, *J. Inorg. Nucl. Chem.*, **24**, 461 (1962).

(9) B. J. Burt and J. F. Kircher, *Radiation Res.*, **9**, 1 (1958).

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

fied by diffusion through a palladium thimble, was added to the sample and the mixture was burned by recirculation over a heated platinum wire. The pressure drop on combustion was a measure of O_2 content and the remainder of the sample was assumed to be N_2 . For samples containing NO, analyses were carried out on an Atlas CH4 mass spectrometer.

Oxides of nitrogen were determined by dissolution of the irradiated samples in 0.1 N NaOH followed by spectrophotometric analysis for nitrite ion at $520 m\mu$ by the α -naphthylamine-sulfanilic acid reagent.¹¹ Expansion of the sample into a previously evacuated bulb of known volume followed by addition of 0.1 N NaOH through a side arm in the bulb gave consistently lower results than expected from stoichiometry. Therefore, 0.1 N NaOH was added directly to the irradiation cell. Although this technique required that cells be disassembled, cleaned, and reassembled after each irradiation, the nitrite yields gave good material balance.

Irradiations. The radiation source was a 1.0-Mev van de Graaff electron accelerator. Irradiation cells for use at room temperature and high-voltage equipment were similar to those used by Meisels.¹⁰ These cells were sufficiently large to permit chemical analysis of the gas and consisted of Pyrex cylinders, 4.11 cm in i.d. and 2.05 cm in length, fitted with amalgamated lead gaskets and 0.013-cm aluminum windows. For irradiations above room temperature, a stainless steel cell 2 in. in diameter and 4 in. in length shown in Figure 1 was fitted at one end with a 0.013-cm aluminum window by means of a compression seal. The window was sealed, without gasket since lead gaskets are unsuitable at high temperatures, between an outer ring and a flange on the cell which had been machined to provide a small raised lip. Ionization currents were measured between the cylindrical cell wall and a tungsten rod projecting axially through a vacuum-tight Kovar seal at one end. The cell was coated outside with a refractory cement and wrapped with electrical heating tape to give temperature uniformity to $\pm 2^\circ$ at 300° as measured by thermocouples imbedded in the refractory cement.

Results

Dosimetry. Application of an electric field during radiolysis induced positive and negative charges to drift to the cathode and anode, respectively. A measurable ion current increases with increasing ratio of the electric field, X , to the pressure, p , until all ions are collected at the windows and a plateau is reached in a plot of ionization current, i , as a function of X/p . The saturation current i_s , measured at the plateau, together with the energy required to produce one ion pair in nitrous oxide ($W_{N_2O} = 32.9^{10}$), is a measure of the rate

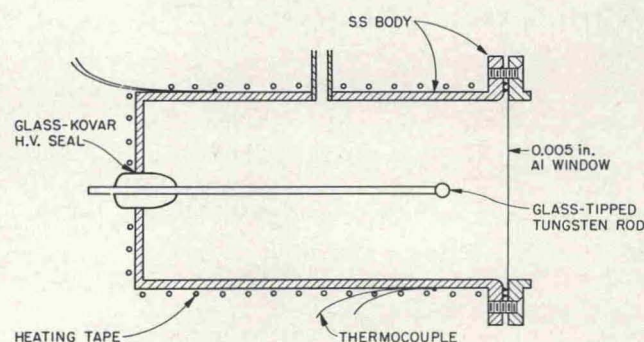


Figure 1. High-temperature irradiation cell.

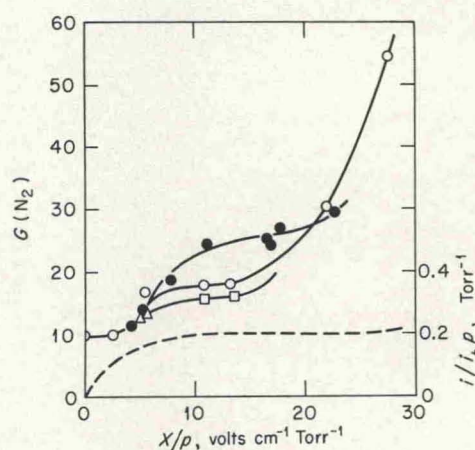


Figure 2. Dependence of $G(N_2)$ on X/p and pressure at 24° . Pressures of N_2O in torr: \bullet , 50; \circ , 100; \square , 200; and Δ , 500.

of energy absorption during radiolysis. Under our experimental conditions, i_s was a linear function of both the accelerator beam current i_b and the pressure. A typical plot of $i/i_b p$ as a function of X/p is shown in Figure 2.

i_s was not measured for the samples in which products of radiolysis were determined. The presence of an electric field during radiolysis markedly affects product formation as shown in Figure 2 for $G(N_2)$ as a function of X/p . There is a striking difference between the effect of an electric field on N_2O and that on C_2H_4 previously reported¹² from this laboratory. The decomposition of C_2H_4 is only slightly affected by an electric field up to $X/p \sim 15$ and then product yields increase sharply with increase in X/p from 15 to the onset of secondary ionization at $27 v cm^{-1} torr^{-1}$. In sharp contrast, there is a stepwise increase in $G(N_2)$ from N_2O at

(11) B. F. Rider and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **18**, 96 (1946).

(12) G. G. Meisels and T. J. Sworski, *J. Phys. Chem.*, **69**, 2867 (1965).

field strengths below $15 \text{ v cm}^{-1} \text{ torr}^{-1}$ superimposed on a further sharp increase in $G(\text{N}_2)$ with increase in X/p from 15 to the onset of secondary ionization. The onset of the first increase occurs at about the same value of X/p for all pressures, but the magnitude of the stepwise increase is highest at the lowest pressure. Since this increase sets in before the ionization current has reached its saturation value i_s , dosimetry measurements should be carried out in the absence of electric fields.

Thus, to determine energy absorption with high accuracy, i_b should be monitored continuously during the irradiation but without application of an electric field. This was accomplished by using a second irradiation cell to monitor i_b , a procedure employed by Boag.¹³ Two identical cells were mounted in tandem in the path of the accelerator beam: the first cell adjacent to the beam port of the accelerator monitored the accelerator beam by a continuous recording of i_s and the second cell was used to determine product yields. Chemical yields were not determined in the first cell and electrical fields were eliminated in the second cell by electrically connecting both windows together to ground. The attenuation of i_b by the first cell was determined in a series of calibration runs by measurement of i_s in both cells simultaneously (using two high-voltage supplies and two X-Y recorders) as a function of nitrous oxide pressure and accelerator beam current. A constant ratio of 0.370 ± 0.001 was determined for the energy absorbed in the second cell relative to the first—at the same N_2O pressures—over the range 22 to 600 torr and independent of i_b . Most of the experiments were carried out with the same N_2O pressure in both cells but it was also ascertained that (a) i_s was directly proportional to N_2O pressure in each cell as shown in Table I and (b) G values measured in the second cell were, within experimental error, independent of N_2O pressure in the first cell, at least from 50 to 200 torr.

Table I: Dependence of i_s/i_b on Pressure

N_2O pressure, torr	Range of i_b , μa	i_s/i_b	$i_s/i_b P$, torr^{-1}
22.0	0.08–8.00	4.29 ± 0.01	0.195 ± 0.001
98.0	0.02–2.00	19.3 ± 0.1	0.197 ± 0.001
147	0.02–1.00	29.0 ± 0.2	0.197 ± 0.001

Effect of Pressure. Primary products in the radiolysis of N_2O are N_2 , O_2 , and NO .¹⁴ A slow, thermal reaction of NO and O_2 to form NO_2 occurs in the gas phase. NO and O_2 react rapidly when the irradiated sample is condensed with liquid N_2 ,⁹ a common practice in analysis for

N_2 and O_2 . G values determined after reaction of NO and O_2 to form NO_2 will be denoted by $G(\text{N}_2)$, $G(\text{O}_2)$, and $G(\text{NO})$.

Values for $G(\text{N}_2)$ and $G(\text{O}_2)$ at 24° and pressures of 50, 200, and 600 torr are listed in Table II. No effect of radiation intensity was observed over at least an eight-fold variation in i_b from 0.5 to $4.0 \mu\text{a}$ [7.5×10^{18} to $6.0 \times 10^{19} \text{ ev g}^{-1} \text{ min}^{-1}$] at 600 torr, or over smaller variations in intensity at other pressures. The results in Table II show a decrease in $G(\text{N}_2)$ at large doses and indicate an initial value for $G(\text{N}_2)$ of 10.0 ± 0.2 independent of pressure, within experimental error, from 200 to 600 torr. Lower values for $G(\text{N}_2)$ at 50 torr are attributed principally to a nonlinearity of $G(\text{N}_2)$ with dose at the higher doses employed, although a slight decrease in $G(\text{N}_2)$ with decrease in pressure cannot be ruled out. $G(\text{O}_2)$, however, markedly decreases with decreasing pressure: $G(\text{O}_2) = 2.0 \pm 0.2$ at 600 torr, $G(\text{O}_2) = 1.5 \pm 0.2$ at 200 torr, and $G(\text{O}_2) = 0.9 \pm 0.1$ at 50 torr.

Effect of Temperature. The stainless steel irradiation cell was used at high temperatures. N_2O in con-

Table II: Dependence of N_2 and O_2 Yields on Pressure^a

Pressure, torr	Dose, 10^{20} ev/g	$G(\text{N}_2)$	$G(\text{O}_2)$
600	0.288	10.1	1.96
	0.361	10.0	2.07
	0.594	10.0	1.82
	0.741	10.1	2.13
	1.12	9.95	2.16
	1.20	9.76	2.04
	1.75	9.49	1.94
200	1.13	10.1	1.64
	1.15	9.92	1.39
	1.44	10.0	1.56
	1.50	10.0	1.50
	2.18	10.2	1.61
	2.91	9.67	1.73
	4.70	9.40	1.79
50	2.94	9.50	0.86
	4.42	9.42	0.96
	5.99	9.25	0.90
	8.55	9.00	0.91
	11.6	9.21	1.07
	17.4	8.84	1.03

^a Irradiations at 24° . Products volatile from trap at -196° .

(13) J. W. Boag in "Radiation Dosimetry," G. J. Hine and G. L. Brownell, Ed., Academic Press Inc., New York, N. Y., 1956, Chapter 4.

(14) G. R. Gedye, *Trans. Faraday Soc.*, **27**, 474 (1931); *J. Chem. Soc.*, 3016 (1931).

tact with stainless steel is stable up to at least 200°. Thermal decomposition and catalytic decomposition on the cell wall becomes serious above 250°. The effect of temperature on the N₂O dosimeter was examined from 24 to 200°.

At low radiation intensities, $i_b \sim 0.005 \mu\text{a}$, it was possible to measure i as a function of X/p by applying a high voltage to the central electrode and measuring the ion current collected on the cell wall. Since the electric field in the cell approximates cylindrical symmetry and because the collection efficiency may be low in certain regions of the cell, i_s could not be determined with the accuracy obtained with the parallel plate electrodes. Nevertheless, at a given density of N₂O, the largest change in i_s observed on increasing the temperature from 24 to 200° was less than 15%. Since this was the limit of accuracy for determinations of i_s in this cell, it was assumed that $W_{\text{N}_2\text{O}}$ is independent of temperature and, likewise, that energy absorption is independent of temperature.

Values for $G(\text{N}_2)$, $G(\text{O}_2)$, and $G(\text{NO})$ as a function of temperature at N₂O density corresponding to a pressure of 400 torr at 24° are listed in Table III. $G(\text{N}_2)$ increases with increase in temperature. $G(\text{O}_2)$ decreases with increase in temperature and is essentially zero at temperatures above 150°. $G(\text{NO})$ is measurable at 150° and increases with increase in temperature.

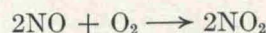
Table III: Dependence of Measured N₂, O₂, and NO Yields on Temperature^a

Temp, °C	$G(\text{N}_2)$	$G(\text{O}_2)$	$G(\text{NO})$
24	10.0	2.0	0.00
70	12.4	1.0	0.00
100	14.1	0.53	0.00
150	17.9	0.03	0.13
200	21.1	0.08	6.20

^a N₂O density corresponding to a pressure of 400 torr at 24°. Products volatile from trap at -196°. Total radiation dose = 0.96×10^{20} ev/g.

Formation of Oxides of Nitrogen.—The yield of oxides of nitrogen was determined by total dissolution of sample in 0.1 N NaOH followed by analysis for the nitrite ion. Nitrite analyses were carried out only at 600 torr of N₂O at doses between 4.28×10^{20} and 12.6×10^{20} ev/g. No effect of dose was observed within the limits of experimental error.

Assuming that NO and NO₂ are the only products of radiolysis besides N₂ and O₂ and that the following reactions go to completion, the yield of oxides of nitro-



gen was measured to be $G(\text{NO} + \text{NO}_2) = 3.9 \pm 0.3$ at 24°.

With $G(\text{N}_2) = 10.0$ and $G(\text{O}_2) = 2.0$, stoichiometry requires that $G(\text{NO} + \text{NO}_2) = 4.0$ in excellent agreement with the observed value. Material balance was, therefore, achieved in this system.

Discussion

Values reported here for $G(\text{O}_2)$ and $G(\text{NO})$ represent only the excess of either O₂ or NO over the amount required by stoichiometry for formation of NO₂. The following relationship is required by stoichiometry.

$$G(\text{NO}_2) = \frac{2}{3}G(\text{N}_2) - \frac{1}{3}G(\text{NO}) - \frac{4}{3}G(\text{O}_2) \quad (\text{I})$$

Initial yields of the primary products of irradiation are denoted by G_{N_2} , G_{NO} , and G_{O_2} . These are related to the observed yields after reaction of NO with O₂ is complete by the relationships II–IV.

$$G_{\text{N}_2} = G(\text{N}_2) \quad (\text{II})$$

$$G_{\text{O}_2} = G(\text{O}_2) + \frac{1}{2}G(\text{NO}_2) \quad (\text{III})$$

$$G_{\text{NO}} = G(\text{NO}) + G(\text{NO}_2) \quad (\text{IV})$$

Effect of Temperature. $G(\text{N}_2) + G(\text{O}_2)$ varies only slightly with increase in temperature up to 150° since an increase in $G(\text{N}_2)$ is accompanied by a decrease in $G(\text{O}_2)$ as shown in Table III. For this reason, N₂O decomposition—measured by the yield of noncondensable gas at liquid N₂ temperature—appears to be temperature independent up to about 150°. When G_{NO} exceeds $2G_{\text{O}_2}$ and $G(\text{NO})$ becomes appreciable, as shown in Table III for 200°, the yield of noncondensable gas will markedly increase with increase in temperature. Thus, the sharp increase in noncondensable gas above 150° previously attributed¹⁵ to an increase in $G(\text{N}_2) + G(\text{O}_2)$ is here attributed to $G(\text{N}_2) + G(\text{NO})$.

G_{N_2} , G_{O_2} , G_{NO} , and $G_{\text{N}_2\text{O}}$ increase with increase in temperature as shown in Figure 3. The results approximate an Arrhenius dependence with apparent activation energies of approximately $E_{\text{N}_2}^a = 1.2$, $E_{\text{O}_2}^a = 0.75$, $E_{\text{NO}}^a = 2.2$, and $E_{\text{N}_2\text{O}}^a = 1.5$ kcal/mole. This effect of temperature is larger than reported by Wourtsel,¹⁶ in good agreement with the results of Flory¹⁵ and less than reported by Gorden and Ausloos.¹⁷

A priori, one would not expect that thermal energy would make a significant contribution to the elemen-

(15) D. A. Flory, *Nucleonics*, 21, No. 12, 50 (1963).

(16) E. Wourtsel, *Radium*, 11, 332 (1919).

(17) R. Gorden, Jr., and P. Ausloos, *J. Res. Natl. Bur. Std.*, A69, 79 (1965).

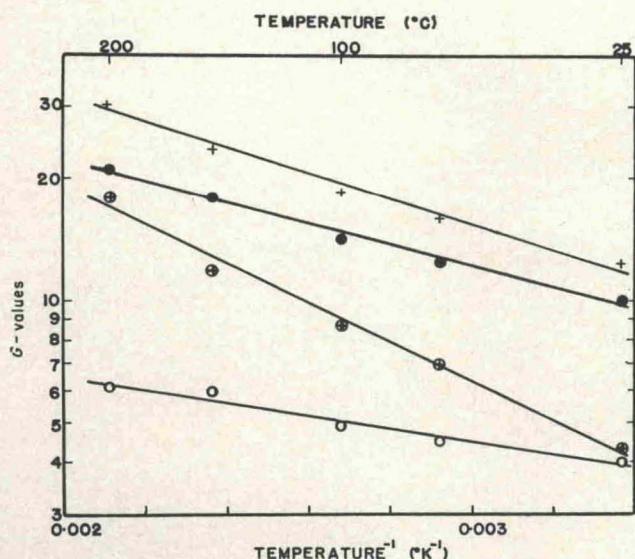
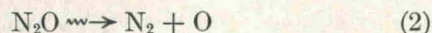
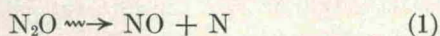
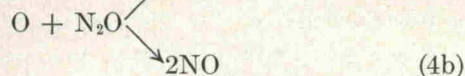
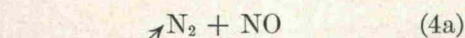
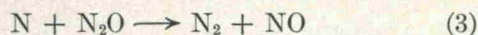


Figure 3. Dependence of initial G values on temperature. N_2O concentrations were constant at 400 torr at 24° : O , G_{O_2} ; \oplus , G_{NO} ; \bullet , G_{N_2} ; and $+$, G_{-N_2O} .

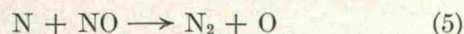
tary processes in radiation chemistry. The marked effect of temperature must be attributed to subsequent reactions of ionic or free-radical intermediates. The net effect of ionization and excitation has been assumed¹⁴ to result in two over-all processes (eq 1 and 2) which have



also been postulated^{18,19} as primary photochemical processes. Reactions of N and O atoms with N_2O (eq 3 and 4) are endothermic if N and O atoms are in the



ground state.²⁰ N atoms react with NO ²¹ (eq 5),



while O atoms must recombine. As the temperature is increased and reactions 3 and 4 become more probable, G_{-N_2O} would increase with a limiting yield at high temperatures equal to twice the value observed at low temperatures.

Figure 3 shows that G_{-N_2O} increases by more than a factor of 2 between 24 and 200° . Gorden and Ausloos¹⁷ report that G_{N_2} increased by almost a factor of 8 between 40 and 376° . These increases are too large to explain by the sequence of reactions 1–4. Gorden and

Ausloos¹⁷ have postulated an ionic chain reaction. Our large increase in the ratio G_{NO}/G_{O_2} with increase in temperature is consistent with their reaction mechanism.

Effect of Pressure. Table IV shows initial yields for 50, 200, and 600 torr N_2O , calculated from the data in Table II. Although Table II does show all values less than 10.0 for $G(N_2)$ at 50 torr, a plot of N_2 concentration against dose shows that all data for 50, 200, and 600 torr fall on the same curve, indicating a common initial yield. While G_{N_2} and G_{-N_2O} remain essentially constant over this pressure range, G_{O_2} decreases and G_{NO} increases as the pressure is lowered. The effect of pressure is to alter the product distribution without affecting G_{-N_2O} .

Table IV: Effect of Pressure on Primary Product Yields^a

Pressure, torr	G_{N_2}	G_{NO}	G_{O_2}	G_{-N_2O}
600	10.0	4.0	4.0	12.0
200	10.0	4.6	3.9	12.3
50	10.0	5.5	3.6	12.7

^a Primary is used here only to denote product yields before secondary reaction of NO with O_2 .

Effects of Electrical Fields. Application of an electrical field causes the thermal electrons to gain energy as a result of diffusive displacements and to acquire a drift velocity in the direction of the field. At values of X/p greater than $25 \text{ v cm}^{-1} \text{ torr}^{-1}$, the energy distribution of these electrons is such that secondary ionization becomes significant, as indicated by the increase in i_s/v_p at $X/p = 30$ in Figure 2. The increase in product G values at values of X/p less than required for the onset of significant secondary ionization is attributable principally to molecular excitations.¹² Typical molecular excitations due to absorption of high-energy radiation lie very high, include superexcited states, and are principally optically allowed states.^{22,23} In sharp contrast, molecular excitations due to collisions with electrons accelerated by an electrical field lie very low, and optically forbidden states become important. For

(18) W. A. Noyes, Jr., *J. Chem. Phys.*, **5**, 807 (1937).

(19) M. Zelickoff and L. M. Aschenbrand, *ibid.*, **22**, 1680 (1954).

(20) J. P. Doering and B. H. Mahan, "Chemical Reactions in the Lower and Upper Atmosphere," Stanford Research Institute Symposium, Interscience Publishers, Inc., New York, N. Y., 1961, Paper No. 21.

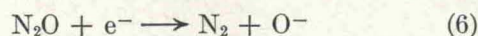
(21) J. P. Doering and B. H. Mahan, *J. Chem. Phys.*, **36**, 1682 (1962).

(22) R. L. Platzman, *Vortex*, **23**, 372 (1962).

(23) R. L. Platzman, *Radiation Res.*, **17**, 419 (1962).

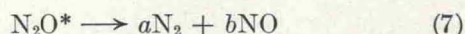
example, the dissociation of H_2 by an electrical field was quantitatively explained by Poole²⁴ with the theory of Emeleus, Lunt, and Meek²⁵ assuming that only triplet states of H_2 ($3\Sigma_g^+$ and $3\Sigma_u^+$) dissociate while singlet states undergo radiative transitions to the ground state.

The large stepwise increase in G_{N_2} and G_{NO} at X/p less than $15 \text{ v cm}^{-1} \text{ torr}^{-1}$ is in qualitative agreement with both the observations of Williams and Essex²⁶ and Burt and Kircher⁹ and their postulate that excitation and dissociation of N_2O is induced by electrons accelerated in an electrical field. However, the further and larger increase in G_{N_2} and G_{NO} with concomitant increase in G_{O_2} from $X/p \sim 15 \text{ v cm}^{-1} \text{ torr}^{-1}$ to the onset of secondary ionization was not observed by either Williams and Essex²⁵ or Burt and Kircher⁹ and is in disagreement with their conclusion that yields would not increase at higher values of X/p . They assumed that all electrons are captured before reaching the electrodes by dissociative electron capture²⁷ (eq 6) and that a limiting ratio of

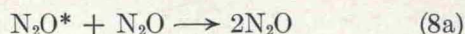


dissociative excitation to dissociative electron capture is reached at X/p less than $15 \text{ v cm}^{-1} \text{ torr}^{-1}$.

If dissociative attachment is the ultimate fate of all electrons in N_2O at the pressures used in this work, then for a given value of X/p the number of excited molecules formed by each electron before attachment should be constant: $G_{N_2O^*} = kG_{e^-}$, where $G_{N_2O^*}$ and G_{e^-} are the numbers of excited N_2O molecules and electrons, respectively, formed per 100 ev absorbed from the accelerator electron beam, and k is a constant which would depend only on X/p . The marked dependence of G_{N_2} and G_{NO} on pressure at $X/p \sim 11$ shown in Figures 2 and 4 indicates collisional deactivation of N_2O^* in competition with the dissociation of N_2O^* which ultimately yields a molecules of N_2 and b molecules of NO .



Assuming deactivation occurs by collision with another



N_2O molecule, then ΔG_{N_2} , the enhancement in G_{N_2} at fixed X/p , should be given by

$$1/\Delta G_{N_2} = A(1 + k_{8a}[N_2O]/k_7) \quad (Va)$$

where $A = akG_{e^-}$ is a constant at fixed X/p and $[N_2O]$ is the pressure in torr. An analogous relationship can be derived for ΔG_{NO} .

On the other hand, if attachment does not occur to any significant extent, then it can be assumed that $G_{N_2O^*} = \alpha_e l G_{e^-}$ where α_e is the number of N_2O^* formed per unit path length by each electron owing to energy

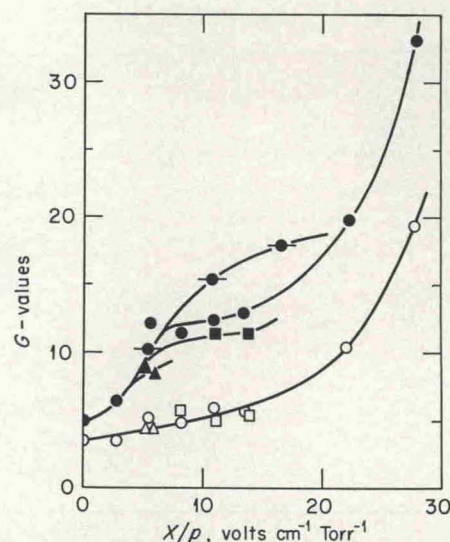
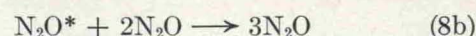


Figure 4. Dependence of G_{NO} (dark symbols) and G_{O_2} (light symbols) on X/p and pressure. Pressures of N_2O in torr: \circ —, 50; \bigcirc , 100; \square , 200; and \triangle , 500.

absorbed from the electrical field, and l is the average path length for electrons in the irradiation cell. Then α_e for excitation is analogous to the "first Townsend coefficient,"²⁸ α_i for ionization and α_e/p should be a function only of X/p , just as is α_i/p . However, the results are quantitatively inconsistent with bimolecular deactivation of N_2O^* since G_{N_2} and G_{NO} would then be expected to increase with increase in pressure. Suppose that collisional deactivation is termolecular, as pro-



posed by Callear and Robb²⁹ for $C_2H_4^*$. Then ΔG_{N_2} at fixed X/p should be given by the following relationship

$$[N_2O]/\Delta G_{N_2} = B(1 + k_{8b}[N_2O]^2/k_7) \quad (Vb)$$

where $B = [N_2O]/aG_{N_2O^*} = [N_2O]/a\alpha_e l G_{e^-}$ is constant as explained above.

The limited data in Figures 2 and 4 preclude quantitative evaluation of the constants in equations Va or Vb. Qualitatively, however, the pressure dependence of ΔG_{N_2} and ΔG_{NO} at $X/p \sim 11$ yields approximate values for k_{8a}/k_7 or k_{8b}/k_7 . Then the lifetime of N_2O^* can be estimated by assuming a value for (a) k_{8a} of

(24) H. G. Poole, *Proc. Roy. Soc. (London)*, **A163**, 424 (1937).

(25) K. G. Emeleus, R. W. Lunt, and C. A. Meek, *ibid.*, **A156**, 394 (1936).

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

(27) N. E. Bradbury and H. E. Tatel, *ibid.*, **2**, 835 (1934).

(28) L. B. Loeb, "Fundamental Processes of Electrical Discharge in Gases," John Wiley and Sons, Inc., New York, N. Y., 1939.

(29) A. B. Callear and J. C. Robb, *Discussions Faraday Soc.*, **17**, 21 (1954).

about $10^{11} M^{-1} \text{ sec}^{-1}$ for bimolecular deactivation or (b) k_{8b} about $10^8 M^{-2} \text{ sec}^{-1}$ assuming termolecular deactivation, as predicted by most treatments³⁰ and assuming 100% efficiency in deactivation. By either of the above treatments, an average lifetime $\tau_{N_2O^*} \sim 1/k_7 \sim 10^{-9} \text{ sec}$ results. The results of the present work are therefore consistent with either electron attachment to N_2O or no significant attachment but a termolecular quenching mechanism.

N₂O Dosimetry. The values of $G(N_2) = 10.0 \pm 0.2$, $G(O_2) = 2.0 \pm 0.2$, and $G(-N_2O) = 12.0 \pm 0.4$ measured for small conversions at 24° and 600 torr are in good agreement with determinations of $G(N_2 + O_2) = 11.9 \pm 0.7$ by Flory,¹⁵ $G(N_2) = 9.7$ by Moseley and Truswell,³¹ $G(-N_2O) = 12.0 \pm 0.3$ by Harteck and Dondes,⁷ and $G(-N_2O) = 12.3 \pm 1.3$ by Gedye.¹⁴ The disagreement with the determinations of $G(N_2) = 12.4 \pm 0.4$ by Johnson⁸ and $G(N_2) = 11.3$ by Burt and Kircher⁹ (both values recalculated on the basis of $W_{N_2O} = 32.9^{10}$) established by the method of ionization currents may be due to the cylindrical geometry of the ionization chambers used by these workers, making it necessary to extrapolate the ionization current to infinite voltage⁸ to obtain a value for the current corre-

sponding to saturation. The collection efficiency in ionization chambers of this design may be quite low,¹³ giving rise to a low apparent dose and high apparent G values. In addition, the problem of circumventing the enhancement in chemical yields which results when a voltage is applied to nitrous oxide under irradiation must also be met. The effects of wall thickness and cell diameter in small cells may be responsible for the differences between the present work and the values $G(N_2) = 11.0 \pm 0.4$, determined by Hearne and Hummel,³² and $G(N_2) = 13.1 \pm 0.2$, determined by Kubose.³³ Wourtsel's¹⁶ original result of 1.74 molecules of N_2O decomposed/ion pair has been corrected to 2.7 by Mund,³⁴ giving a value of $G(-N_2O) = 8.2$ which is considerably lower than any other thus far reported.

(30) See, for example, L. S. Kassel, "The Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., New York, N. Y., 1932.

(31) F. Moseley and A. E. Truswell, Atomic Energy Research Establishment, Harwell, England, Report No. AERE-R 3078 (1960).

(32) J. A. Hearne and R. W. Hummel, *Radiation Res.*, **15**, 254 (1961).

(33) D. Kubose, *Trans. Am. Nucl. Soc.*, **7**, 318 (1964).

(34) W. Mund, *J. Phys. Chem.*, **30**, 890 (1926).