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COBALT-60 GAMMA RADIOLYSIS OF LIQUID DINITROGEN TETROXIDE

THOMAS C. CASTORINA

MAY 1963

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BY

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ABSTRACT

The cobalt-60 gamma radiolysis of liquid dinitrogen tetroxide $(N_2O_4)_l$ has been investigated as a function of variations in temperature, gas-to-liquid volume ratio, dose rates, and method of $(N_2O_4)_l$ purification. The radiolytic products are shown to be N_2, N_2O, and N_2O_5. The material balance of the O_2 released at post-irradiation thermal equilibrium as compared with the calculated O_2 derived from the production of N_2 and N_2O from N_2O_4 is good to within 10%. $(N_2O_4)_l$ is relatively radiation-resistant, having a G value of only 0.075, the ratio of N_2 and N_2O product formation being 2:1. The independence of product yields in relation to changes in dose rate indicates that radical-molecule processes are involved in product formation. An apparent induction period, observed at 0.4 Mrad per hour, is also shown to be independent of dose rate. The addition of argon to $(N_2O_4)_l$ has no effect on the radiolytic yields. The addition of O_2, over the partial pressure range of 200-350 mm, results in a G value for N_2O_5 formation that is in excellent agreement with that for N_2O_5 formation from pure $(N_2O_4)_l$. Although the addition of O_2 has no effect on the N_2O formation, the induction period for N_2 is eliminated and the amount of N_2 is decreased by 80%.

INTRODUCTION

The nitro group is considered to be one of the most important plosophoric groups in Ordnance chemistry. When substituted in an organic molecule in sufficient numbers, it supplies the necessary oxygen balance for the complete conversion of the carbons and hydrogen to carbon dioxide and water. The problem has been to effect the maximum number of substitutions possible without degrading the parent molecule in the process. Conventional methods of synthesis are rapidly exhausting all avenues of approach to a solution to this problem. New methods must be investigated, one such method being preparative radiation chemistry.

High-energy radiation is known to produce the already familiar entities, carbonium and nitronium ions, free radicals and excited molecules in environments devoid of high pressures and temperatures, stringent oxidizers and catalysts. This might make possible modifications and improvements in existing methods of synthesis that depend on their reactions. Even more important, however, is the possibility that high-energy radiation, e.g., cobalt-60 gammas, may afford a unique method of forming different active intermediates, capable of undergoing new types of reactions not so much in quantity but in kind as an indication that the resultant new compounds can and do exist. Since NO_2 normally exists in equilibrium with dinitrogen tetroxide, it is more than likely that liquid dinitrogen tetroxide $(N_2O_4)_l$ when subjected to ionizing radiation could become a good source not only of NO_2 radicals but of ionic and excited NO_2 molecules as well. The concurrent existence of such a variety of active intermediates in situ may open a whole new field of nitrolysis.

Before a study can be made of a two-component system, as would be the case in preparative radiation chemistry, the radiolysis of each component should be studied separately. For a two-component system consisting of benzene and $(N_2O_4)_l$, only one of the components needs investigation. The radiation chemistry of benzene is fairly well established and benzene has been found to be relatively resistant to gamma fields (Ref 1). However, the radiolysis of nitrogen dioxide, in its dimeric form, as a liquid, has not been reported in the literature. The radiolysis of nitrogen dioxide gas in a nuclear reactor has been studied by Harteck and Dondes (Ref 2) and, more recently, Dimitriev and Saradzhev (Ref 3) have reported on the gamma radiolysis of gaseous N_2O_4 at varying intensities and pressures. For the present study, an investigation of the cobalt-60 gamma radiolysis of $(N_2O_4)_l$ was considered more appropriate to subsequent investigations involving its radiation-induced reactions with aromatics and possibly aliphatics. Diamagnetic $(N_2O_4)_l$ is transparent over a wide range of wavelengths. The series of light straw to brown-red colors imparted to the liquid is due to the presence of the paramagnetic NO_2 monomer. In the saturated vapor phase, N_2O_4 dissociates 8.6% at -11.2° C (MP) and 15.9% at 21.2° C (BP). In the liquid phase, the dissociation of N_2O_4 occurs to the extent of 0.018% at -11.2° C and 0.12% at 21.2° C (Ref 4).

DISCUSSION AND RESULTS

Using tank gas, $(N_2O_4)_l$ of high purity was prepared by sparging with purified oxygen to convert lower oxides to N_2O_4. Trace quantities of moisture were removed with phosphorus pentoxide. The liquid was degassed a minimum of three times at -78° C. The center fractions, which were protected from stopcock grease contamination by glass bead traps, were distilled into 5-cc pyrex break seals for irradiation studies. Samples were irradiated at 20° C in a cobalt-60 gamma field of approximately 4×10^5 r/hr.

The irradiated samples were degassed at liquid nitrogen temperature (-196° C) and the gases isolated at this temperature were analyzed mass spectrometrically and found to consist of only nitrogen and oxygen. The relative amounts of each constituent were calculated from their respective mass peak heights. As a check, the amount of oxygen was also determined by its reaction with hydrogen at the catalyzing surface of a heated (barely perceptible glow point) platinum filament. The results listed in Table 1 show the two methods to be in good agreement.

In the process of making these initial determinations, 5 to 6 sample batches of $(N_2O_4)_l$ had been irradiated together for the same period of time. Upon removal from the source they were placed under refrigeration at 2-5° C and taken as needed for analysis over a period of 2 days. When this was done, it was observed that the percentage of oxygen gradually increased with each successive sample analysis. This was indicative of the existence of a thermally unstable product of radiolysis which decomposed with the evolution of oxygen. In establishing the post-irradiation gaseous product(s) of thermal decomposition the following assumptions were made: (a) that oxygen was the only gas released after radiation, and (b) that nitrogen was a direct product of radiolysis, independent of the amount of oxygen present at any one time after radiolysis. To demonstrate the validity of these assumptions, an extensive series of $(N_2O_4)_l$ samples were irradiated with various doses. The irradiated samples were analyzed at irregular intervals during the post-irradiation

TABLE 1

Comparative Analysis of Gaseous Products Isolated at -196° C

Platinum Filament Analysis[a]		Mass Spectrometric Analysis[b]	
Percent Oxygen	Percent Nitrogen	Percent Oxygen	Percent Nitrogen
3.6	96.4	3.5	96.5
3.4	96.6	3.6	96.4
5.7	94.3	6.5	93.5
5.4	94.6	6.4	93.6
3.6	96.4	5.7	94.3
25.8	74.2	26.0	74.0
43.5	56.5	44.8	55.2
50.7	49.3	50.9	49.1
65.3	34.7	66.9	33.1
65.5	34.5	65.7	34.3

---

[a] Percent composition of N_2 by difference

[b] Based on relative ratios of respective mass peaks. (N_2 and O_2 were the only gases present.)

period. The random distribution of oxygen was subtracted from the gas mixture isolated at -196°C and all values were reported in terms of nitrogen formed. These results are listed in Table 2. A plot of the cc of N_2 at STP per gram of $(N_2O_4)_l$ versus the dose in megarads is given in Figure 1. The curve obtained shows an apparent induction period which may represent that time interval where intermediate species are increasing in sufficient concentrations for final conversion to stable radiolytic products. It is also possible that this induction period is due to the presence of trace quantities of impurities which are scavenging the intermediates, momentarily preventing the formation of products of radiolysis. Following this induction period there is a straight line portion of the curve from 15 to 50 megarads corresponding to a constant G (N_2) of 0.052. This constant G value demonstrates the independence of N_2 product formation from variations in the amount of O_2, and thereby demonstrates further that N_2 is a direct product of radiolysis. It was therefore concluded that the post-irradiation thermal decomposition of one of the products of radiolysis involves the evolution of O_2 only.

At the outset of this work, extreme difficulty was experienced in preparing ampoules of liquid N_2O_4 devoid of free space. This was due to the relatively high thermal coefficient of expansion of $(N_2O_4)_l$, 2.4×10^{-3}cc increase per unit cc per degree centigrade rise (greater than that of ethyl ether). It therefore became necessary to determine the effect of the presence of various volumes of gas in equilibrium with the liquid on the G values and mechanism of product formation. G value is defined as the number of molecules, either decomposed or formed, per 100 electron volts of energy absorbed. Table 3 shows that the G (N_2) is independent of variations in the ratio of gas-to-liquid volumes over a factor range of approximately 600. The ratio of 0.004 represents a liquid sample with a volume of 0.02 cc of gas confined in the one mm capillary end of the break-seal. It was therefore concluded that in calculating G values, variations in the volume of gas in equilibrium with the liquid could be ignored, where the weight of the gas is always negligible in comparison with that of the liquid. The calculation of the G value, based on the ferrous sulfate dosimeter was, as a result, corrected only for the electron density difference of $(N_2O_4)_l$. In addition, the data listed in Table 3 signifies that nitrogen formation is derived from a liquid intermediate since the G (N_2) remains constant as the volume of gas increases.

To determine how critical the control of temperature is during long periods of irradiation, a series of samples of $(N_2O_4)_l$ was irradiated at

TABLE 2

Independence of N_2 Formation With Variations in the Concentration of Oxygen

Hours Irradiation	Dose M rads	Grams $(N_2O_4)_1$	cc (N_2) STP per g $(N_2O_4)_1$	cc (O_2) STP per g $(N_2O_4)_1$
12	4.92	6.326	0.0012	0.0001
12	4.92	5.991	0.0005	0.0001
24	9.84	6.500	0.0034	0.0001
24	9.84	6.225	0.0035	0.0091
36	14.76	6.324	0.0078	0.0005
36	14.76	6.176	0.0074	0.0082
48	19.68	5.768	0.0123	0.0005
48	19.68	6.187	0.0122	0.0459
72	29.52	6.190	0.0276	0.0770
72	29.52	6.178	0.0279	0.0025
96	39.36	5.934	0.0365	0.0987
96	39.36	5.855	0.0365	0.0152
96	42.14	2.423	0.0418	0.0434
96	42.14	6.161	0.0421	0.0914
96	42.14	5.577	0.0410	0.0121
120	49.20	6.305	0.0490	0.0139
120	49.20	5.420	0.0546	0.1296
120	49.20	6.095	0.0485	0.0132
120	52.68	5.082	0.0566	0.0140
120	52.68	5.184	0.0562	0.1246

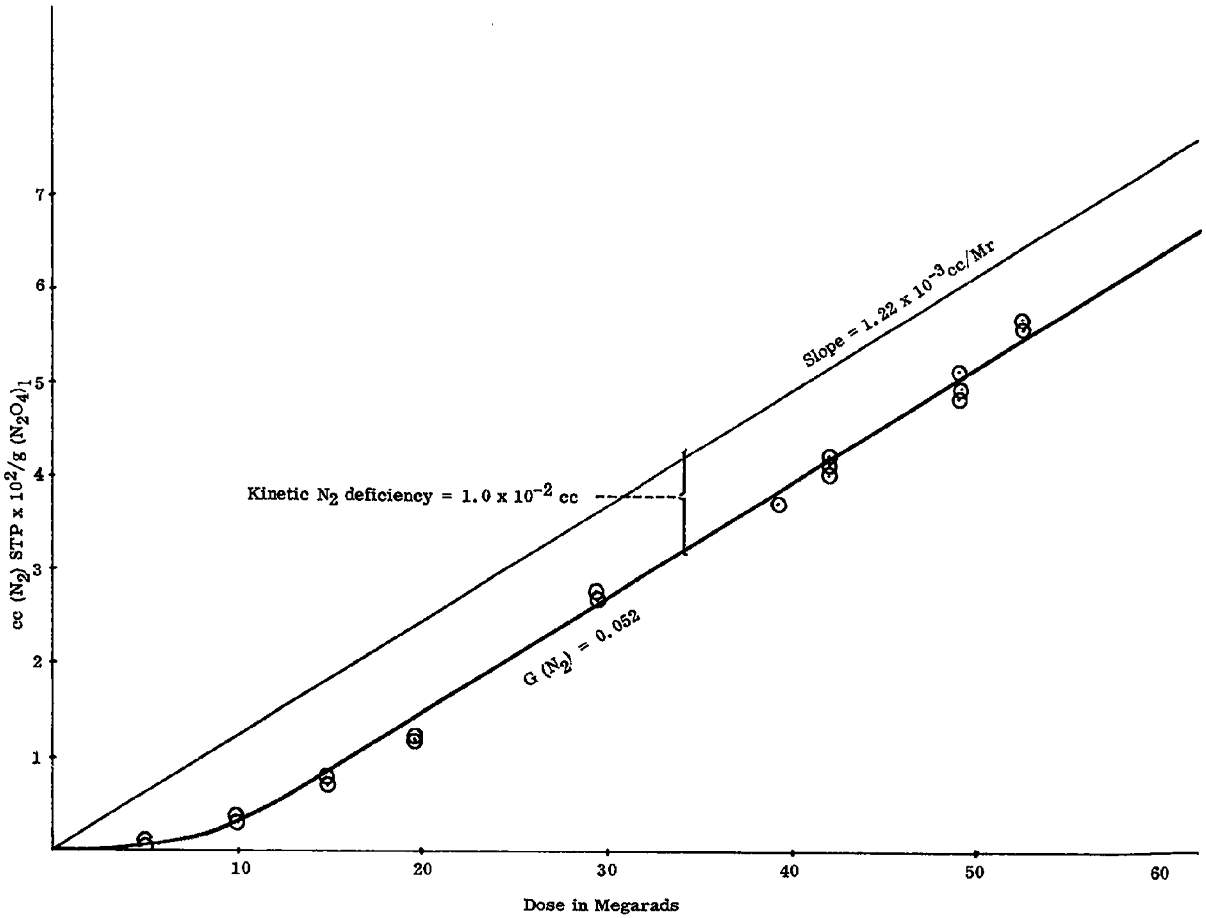


Figure 1. Cobalt-60 Gamma Radiolysis of Liquid N_2O_4 at 20° C. Dependence of Nitrogen Formation on Dose

TABLE 3

Independence of $G(N_2)$ in Relation to Variations in Volume $(N_2O_4)_g$: Volume $(N_2O_4)_l$ Ratio

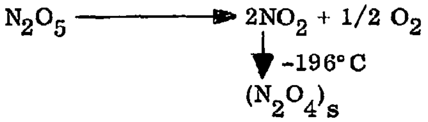
Dose in Rads (x 10^{-7})	$G(N_2)$	Vol $(N_2O_4)_g$: Vol $(N_2O_4)_l$
4.92	0.048	0.031
4.92	0.047	0.050
4.92	0.053	0.100
5.27	0.051	0.307
5.27	0.051	0.348
4.21	0.048	0.877
4.21	0.047	2.318
4.21	0.049	0.952
4.21	0.047	1.637
4.21	0.046	0.114
4.21	0.048	0.035
2.18	0.045	0.004

Average $G(N_2) = 0.048 \pm 0.002$

at different temperatures. The G (N_2) was observed to remain constant over a temperature range of 0° to 30°C. The results of these experiments are summarized in Table 4. However, in spite of this apparent insensitivity of G (N_2) to temperature fluctuations in this range, irradiations throughout this investigation were conducted at 20°C ± 1°.

Kinetics of N_2O_5 Decomposition in $(N_2O_4)_l$

In consideration of the fact that some oxides of nitrogen are thermally unstable at room temperature, all oxides lower than nitrogen dioxide were ruled out. For example, nitrous oxide (N_2O) is especially stable at these temperatures and nitric oxide (NO) as well as N_2O_3 combine readily with the available oxygen of irradiated samples to form NO_2 and/or N_2O_4. On the basis of the results shown in Table 2, this oxide decomposes to O_2 plus some product condensible at -196°C, i.e., the temperature at which the degassing of samples is performed. This would be analogous to:



$$\begin{tikzcd} N_2O_5 \arrow[r] & 2NO_2 + 1/2\ O_2 \arrow[d, "-196^\circ C"] \\ & (N_2O_4)_s \end{tikzcd}$$

(1)

The original studies on the rate of decomposition of nitrogen pentoxide are classics in the field of kinetics and the reaction is reported to be first order over a wide range of temperatures and pressures. As a standard for comparison in the process of identifying the unknown kinetically, Eyring and Daniels' published data on the decomposition of N_2O_5 in $(N_2O_4)_l$ was used (Ref 5). The rates of decomposition based on the rates of oxygen evolution after radiolysis were determined at 20°, 22°, and 25°C, on sets of five samples. Each set was irradiated together for a total of 96 hours, equivalent to 4×10^7 rads. Included with this set was one sample which was quenched in a dry-ice bath directly upon removal from the source. Analysis of this sample gave the concentration of N_2O_5 at zero time after irradiation. A second sample was included that gave the total concentration of the N_2O_5 for the set, upon thermal equilibration. For each particular run, the five samples were placed in a constant temperature bath directly after radiolysis and removed from time to time for oxygen analysis. This data, in terms of cc (O_2) STP per gram of $(N_2O_4)_l$ as a function of time, together with the corresponding fractions remaining (assumed to be N_2O_5), is shown in Table 5. The fraction of N_2O_5 remaining, plotted on the logarithmic scale versus the time in hours, is shown in Figure 2. The straight lines obtained on this semilog plot for each of the temperatures studied indicate first order kinetics.

TABLE 4

Independence of G (N_2) in Relation to Radiolysis of (N_2O_4)$_1$ at Various Temperatures

Dose in Megarads	Temp °C ± 1°	G (N_2)	Average G(N_2)	Average Deviation
39.36	0	0.048	0.047	± 0.001
39.36	0	0.048		
39.36	0	0.047		
39.36	0	0.047		
39.36	0	0.046		
39.36	15	0.045	0.048	± 0.003
39.36	15	0.045		
49.20	15	0.048		
49.20	15	0.053		
42.14	20	0.047	0.048	± 0.001
42.14	20	0.049		
42.14	20	0.047		
42.14	20	0.048		
49.20	20	0.047		
52.68	20	0.051		
26.40	30	0.049	0.048	± 0.001
26.40	30	0.047		

TABLE 5

Post Irradiation Rate of N_2O_5 Decomposition as a Function of Temperature [a]

°C ± 0.05	mm Gas (N_2+O_2)	Percent O_2	Grams $(N_2O_4)_l$	$\frac{cc(O_2)\ STP}{g\ (N_2O_4)_l}$ (x 10^2)	°K	Fraction N_2O_5 Remaining[b]	Seconds (x 10^{-4})	Spec Rate Const. (x 10^4 sec^{-1})	
20	118.2	31.8	7.052	1.96	294.5	0.820	0^c	-----	
20	140.5	47.5	7.025	3.48	296.6	0.681	1.8	0.103	$\overline{0.103}$
20	173.8	53.7	7.010	4.87	295.8	0.554	3.6	0.106	
20	189.5	62.3	6.490	6.68	295.4	0.387	7.2	0.104	
20	179.2	65.7	5.400	7.98	296.0	0.268	10.8	0.103	
20	246.0	68.5	6.887	9.00	295.5	0.176	16.2	0.100	
20	263.0	72.5	6.420	10.90	295.4	0	$\rightarrow\infty$ [d]	-----	
22	84.8	19.4	5.730	1.035	297.5	0.902	0^c	-----	
22	102.0	36.2	5.595	2.40	297.5	0.773	1.08	0.14	$\overline{0.14}$
22	145.4	53.2	5.895	4.78	297.2	0.547	3.24	0.15	
22	180.0	60.4	6.150	6.46	296.7	0.389	6.48	0.13	
22	202.2	65.4	6.123	7.84	298.2	0.257	9.72	0.13	
22	235.6	69.6	6.270	9.58	296.4	0.098	16.2	0.14	
22	244.0	71.6	6.038	10.56	297.0	0	$\rightarrow\infty$ [d]	-----	
25	78.0	20.1	5.300	1.08	296.5	0.905	0^c	-----	
25	128.2	52.3	5.230	4.67	297.5	0.588	1.8	0.24	$\overline{0.24}$
25	157.6	62.0	5.310	6.72	297.0	0.408	3.24	0.25	
25	200.5	68.0	5.500	9.06	296.2	0.202	6.48	0.23	
25	218.0	70.6	5.470	10.25	297.0	0.097	9.72	0.23	
25	235.7	71.9	5.580	11.10	296.5	0.022	16.2	0.23	
25	241.2	72.2	5.510	11.35	296.0	0	$\rightarrow\infty$ [d]	-----	
25	91.0	14.0	7.200	0.646	296.0	0.935	0^c	-----	
25	160.7	50.8	7.314	4.09	295.2	0.589	1.8	0.25	$\overline{0.24}$
25	182.0	61.0	6.817	5.99	294.6	0.398	3.6	0.24	
25	227.0	65.5	7.300	7.42	297.0	0.254	5.4	0.24	
25	250.5	69.5	7.483	8.52	296.2	0.144	8.28	0.23	
25	267.0	72.0	7.050	9.95	297.2	0	$\rightarrow\infty$ [d]	-----	

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[a] All samples irradiated simultaneously for 96 hours (4.1 x 10^5r/hr).

[b] In terms of cc $(O_2)/_g\ (N_2O_4)_l$ evolved with time, relative to the amount evolved at t $\rightarrow\infty$.

[c] Quenched in dry-ice bath directly after removal from source.

[d] Thermally equilibrated 7 days at 25° C.

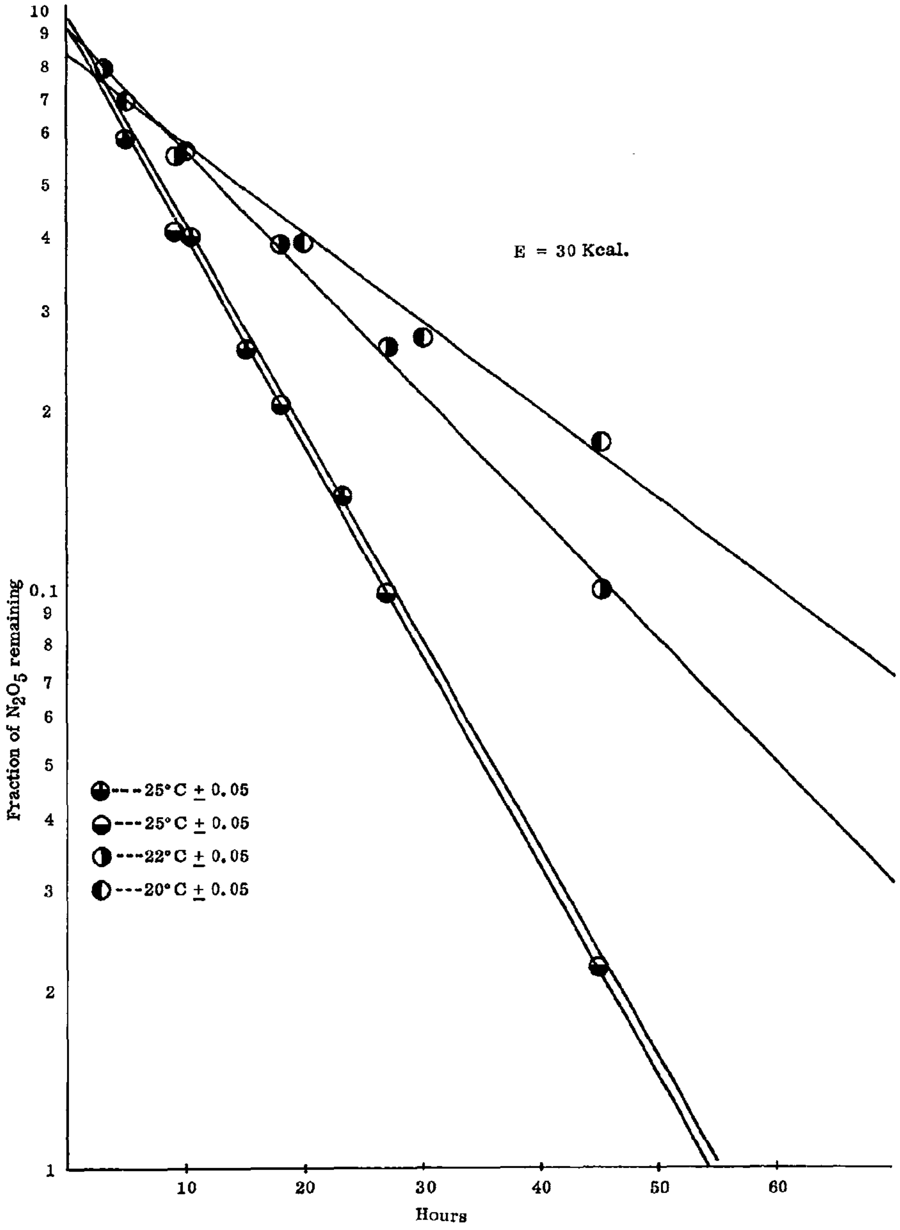

Figure 2. Post Irradiation Rate of N_2O_5 Decomposition as a Function of Temperature

As a check, the kinetics of decomposition of synthetic solutions of N_2O_5 in $(N_2O_4)_1$ were determined and compared to those obtained by Eyring and Daniels. Synthetic solutions were prepared by ozonizing pure $(N_2O_4)_1$ just sufficiently to give millimolar concentrations of N_2O_5, comparable to those of the irradiated samples, here again assumed to be N_2O_5. The solutions were then degassed twice at -78° C and transferred to radially arranged ampoules connected to a common center. The ampoules were finally flame-sealed, placed in a constant temperature bath, and removed from time to time for oxygen analysis. The reproducibility of the sample preparations is shown by the data listed in Table 6. The rates of N_2O_5 decomposition in such concentrations were determined at 20° and 25° C in the same manner as for the irradiated $(N_2O_4)_1$ samples. Table 7 lists the rates of O_2 evolution and related N_2O_5 decompositions. A plot of the log of the fraction of N_2O_5 remaining versus time (Fig 3) also shows first order kinetics.

The specific rate constants were calculated directly from the data rather than from the curves, using the first order expression. This was done for both the irradiated and synthetic solutions and results were found to be constant to within 5%.

Table 8 gives a comparison of these specific rate constants. At 20° C, the average rate constant of the synthetic solutions is in very good agreement with that of the irradiated samples. The higher value reported by Eyring and Daniels is attributed to a concentration effect. At the time their work was reported, the decomposition of N_2O_5 was thought of as a unimolecular first order reaction. Since then, the reaction has been shown by Ogg (Ref 6) to be a complex one, as follows:

$$N_2O_5 \underset{2}{\overset{1}{\rightleftarrows}} NO_2 + NO_3 \tag{2}$$

$$NO_2 + NO_3 \xrightarrow{3} NO + O_2 + NO_2 \tag{3}$$

$$NO + NO_3 \xrightarrow{4} \underset{\substack{\downarrow\uparrow \\ N_2O_4}}{2NO_2} \tag{4}$$

Empirically, Eyring and Daniels did find an apparent concentration effect in carbon tetrachloride solutions of N_2O_5 in that more dilute concentrations decompose at slower rates. It will be noticed that the activation energies in all three cases compare favorably. These kinetic data

TABLE 6

Reproducibility of Sample Preparation of Synthetic Solutions of N_2O_5 in $(N_2O_4)_1$

No. Moles N_2O_5 (x 10^4) per sample Vol., cc	Milli Molar Concentration of N_2O_5 in $(N_2O_4)_1$	Average Per-cent Deviation
0.434/4.13	10.5	2.3
0.368/3.63	10.1	
0.370/3.78	9.8	
0.754/3.55	21.2	2.8
0.638/3.17	20.1	
0.250/4.30	5.8	1.7
0.238/4.21	5.7	

TABLE 7

Rate of Decomposition of Synthetic Solutions of N_2O_5 in (N_2O_4) with Temperature

°C ± 0.05°	mm Gas (N_2+O_2)	mM N_2O_5	Grams $(N_2O_4)_l$	$\frac{\text{cc } (O_2) \text{ STP}}{g(N_2O_4)_l}$ (x 10^2)	°K	Fraction N_2O_5 Remaining[b]	Seconds (x 10^{-4})	Spec. Rate Const. (x 10^4 sec $^{-1}$)	
20	0	0[a]	5.280	0	297.0	1.0	$\rightarrow \infty$ [c]	-----	
20	116[d]	4.0	5.077	0.32	296.6	0.814	1.8	0.12	$\overline{0.12}$
20	182	4.0	5.166	0.76	297.5	0.558	4.32	0.14	
20	212	4.0	5.128	1.05	296.5	0.386	8.64	0.11	
20	242	4.0	5.380	1.29	297.4	0.250	12.96	0.11	
20	273	4.0	5.16	1.72	296.0	0	$\rightarrow \infty$ [c]	-----	
20	0	0[a]	6.180	0	297.0	1.0	$\rightarrow \infty$ [c]	-----	
20	12.5[e]	7.4	6.110	0.748	295.0	0.867	1.08	0.14	$\overline{0.12}$
20	36.0	7.4	6.202	2.13	296.0	0.622	3.60	0.11	
20	57.0	7.4	6.541	3.19	296.0	0.434	7.20	0.12	
20	76.0	7.4	6.510	4.27	297.0	0.243	12.96	0.11	
20	105.0	7.4	6.784	5.64	297.0	0	$\rightarrow \infty$ [c]	-----	
25	0	0[a]	6.020	0	297.0	1.0	$\rightarrow \infty$ [c]	-----	
25	17.0[e]	3.0	5.550	1.12	297.0	0.524	1.8	0.36	$\overline{0.35}$
25	26.0	3.0	5.530	1.73	295.0	0.264	3.6	0.37	
25	31.0	3.0	5.710	1.98	297.0	0.157	5.4	0.34	
25	36.5	3.0	6.230	2.15	295.3	0.082	7.2	0.35	
25	37.0	3.0	5.980	2.24	297.0	0.046	9.0	0.34	
25	38.0	3.0	5.906	2.35	297.2	0	$\rightarrow \infty$ [c]	-----	

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[a] Control - pure $(N_2O_4)_l$.

[b] In terms of cc (O_2)/g $(N_2O_4)_l$ evolved with time, relative to the amount evolved at t $\rightarrow \infty$.

[c] Thermally equilibrated for 7 days at 25° C.

[d] Pressure readings taken at capillary end of McLeod guage.

[e] Pressure adjusted to 2.39 cc volume.

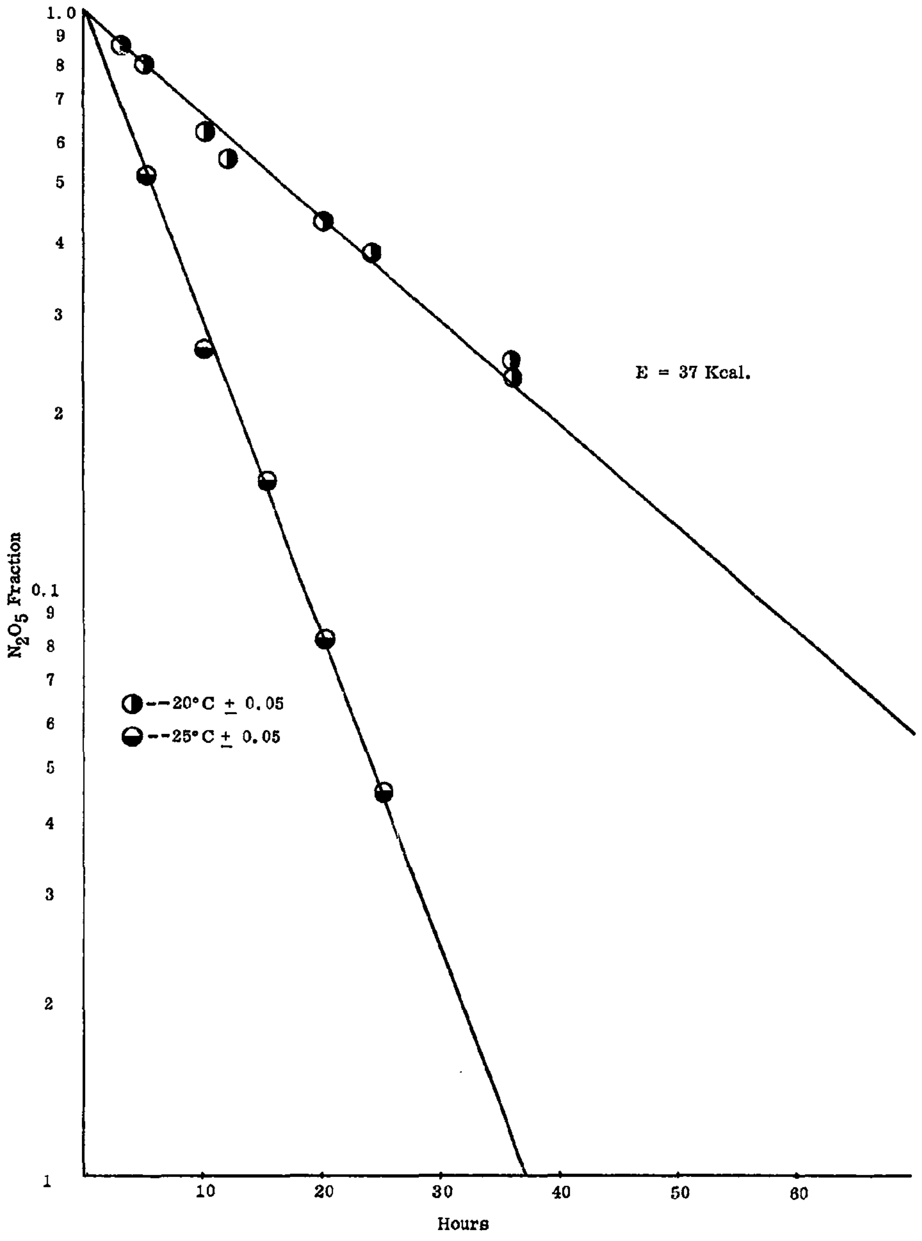

Figure 3. Rate of Decomposition of $\overline{4.8}$ m M Solution of N_2O_5 in $(N_2O_4)_l$ as a Function of Temperature

TABLE 8

Comparative Specific Rate Constants of N_2O_5 Decomposition in $(N_2O_4)_l$ for Synthetic and Radiolytic Solutions[a]

Synthetic Solution of N_2O_5 in $(N_2O_4)_l$ Specific Rate Constant[b] (x 10^4 sec^{-1})		Radiolytic Solution of N_2O_5 in $(N_2O_4)_l$ Specific Rate Constant (x 10^4 sec^{-1})		
20° C ± 0.05°	25° C ± 0.05°	20° C ± 0.05°	22° C ± 0.05°	25° C ± 0.05°
0.14	0.36	0.10	0.14	0.24
0.11	0.37	0.11	0.15	0.25
0.12	0.34	0.10	0.13	0.23
0.11	0.35	0.10	0.13	0.23
0.12	0.34	0.10	0.14	0.23
0.14		0.11[c]		0.25
0.11				0.24
0.11				0.24
				0.23
Avg = 0.12	Avg = 0.35	Avg = 0.10	Avg = 0.14	Avg = 0.24
E = 37 kcal		E = 30 kcal		

---

[a] Calculations based on remaining fraction of N_2O_5 derived from cc (O_2)/gm $(N_2O_4)_l$ evolved with time relative to amount evolved at $t \rightarrow \infty$.

[b] Eyring and Daniels report 0.344 x 10^{-4} sec^{-1} at 20° C and E = 26 kcal for 0.2M solutions of $N_2O_5/(N_2O_4)_l$.

[c] Nitrogen sparged.

clearly establish the identity of the thermally unstable product of liquid N_2O_4 radiolysis to be N_2O_5. The slight increase in k for the synthetic solutions as compared to the irradiated solutions might result from the presence of some unreacted ozone remaining in the synthetic solutions.

Notwithstanding the substantial kinetic evidence for the presence of N_2O_5 attempts were made to identify N_2O_5 directly in situ. However, by virtue of the m Molar concentrations of N_2O_5 involved in this study, together with its chemical instability, direct analysis proved most difficult. The methods of analysis employed included Electron Paramagnetic Resonance (EPR) and Vapor Phase Chromatography (VPC). Both irradiated samples and synthetic solutions of N_2O_5 in $(N_2O_4)_1$, after twelve successive fractionations, failed to show differences in their respective VPC spectra from a reference standard consisting of $(N_2O_4)_1$ alone. The EPR spectra obtained for these samples at -196° C are extremely complex and can be interpreted only by means of detailed calculations.

It had been noted earlier in this work that the percent of oxygen at near zero time after 48 hours of irradiation was only 3.5%. This suggests the possibility that the rate of decomposition of N_2O_5 is initially repressed in a gamma field where the velocity of the reverse reaction is faster than that of the forward reaction

$$5\ N_2O_4 \rightsquigarrow N_2 + 4N_2O_5 \qquad (5)$$

$$2\ N_2O_5 \xrightarrow{k_f} 2N_2O_4 + O_2 \qquad (6)$$

$$2\ N_2O_4 + O_2 \overset{k_r}{\rightsquigarrow} 2N_2O_5 \qquad (7)$$

where $k_r > k_f$.

This rate of N_2O_5 decomposition during irradiation at 20° ± 1° C was determined by quenching the thermal reaction in a dry ice bath directly after removal from the source (designated: zero-time-after-radiolysis) at various time intervals and analyzing for the fraction of N_2O_5 remaining. The data shown in Table 9 gives the rate of oxygen evolution with the relative fractions of N_2O_5 remaining as a function of irradiation time. A graphical representation of this rate in comparison to the rate at the same temperature after radiation (shown in Figure 4) forcefully demonstrates the stabilizing effect of gammas on N_2O_5 in $(N_2O_4)_1$.

TABLE 9

Rate of N_2O_5 Decomposition During Irradiation[a] at 20° C ± 1.0°

Grams $(N_2O_4)_1$	mm Gas (N_2+O_2)	Percent O_2	°K	$\frac{cc(O_2)\ STP}{g\ (N_2O_4)_1(x\ 10^2)}$	Seconds $(x\ 10^{-4})$	Fraction[b] N_2O_5 rem.
5.830	21.4	7.0	296.5	0.10	17.28	0.978
7.070	122.0	72.0	296.1	4.50	$\rightarrow \infty^c$	0
6.178	50.5	8.5	296.3	$\overline{0.27}$	25.92	0.964
6.190	50.2	9.6	297.8			
7.154	202.0	71.6	296.0	750	$\rightarrow \infty^c$	0
6.161	81.8	13.2	296.5	$\overline{0.81}$	34.56	0.926
4.525	59.0	20.5	294.5			
5.510	241.2	72.2	296.0	11.35	$\rightarrow \infty^c$	0
5.082	99.8	22.0	296.2	$\overline{1.48}$	43.20	0.901
5.184	99.5	19.5	296.4			
6.500	348.3	71.9	296.7	14.06	$\rightarrow \infty^c$	0

---

[a] At a dose rate of 0.41 Mrad/hr.

[b] In terms of cc $(O_2)/g(N_2O_4)_1$ evolved with time relative to the amount evolved at $t \rightarrow \infty$

[c] Thermally equilibrated for 7 days at 25° C.

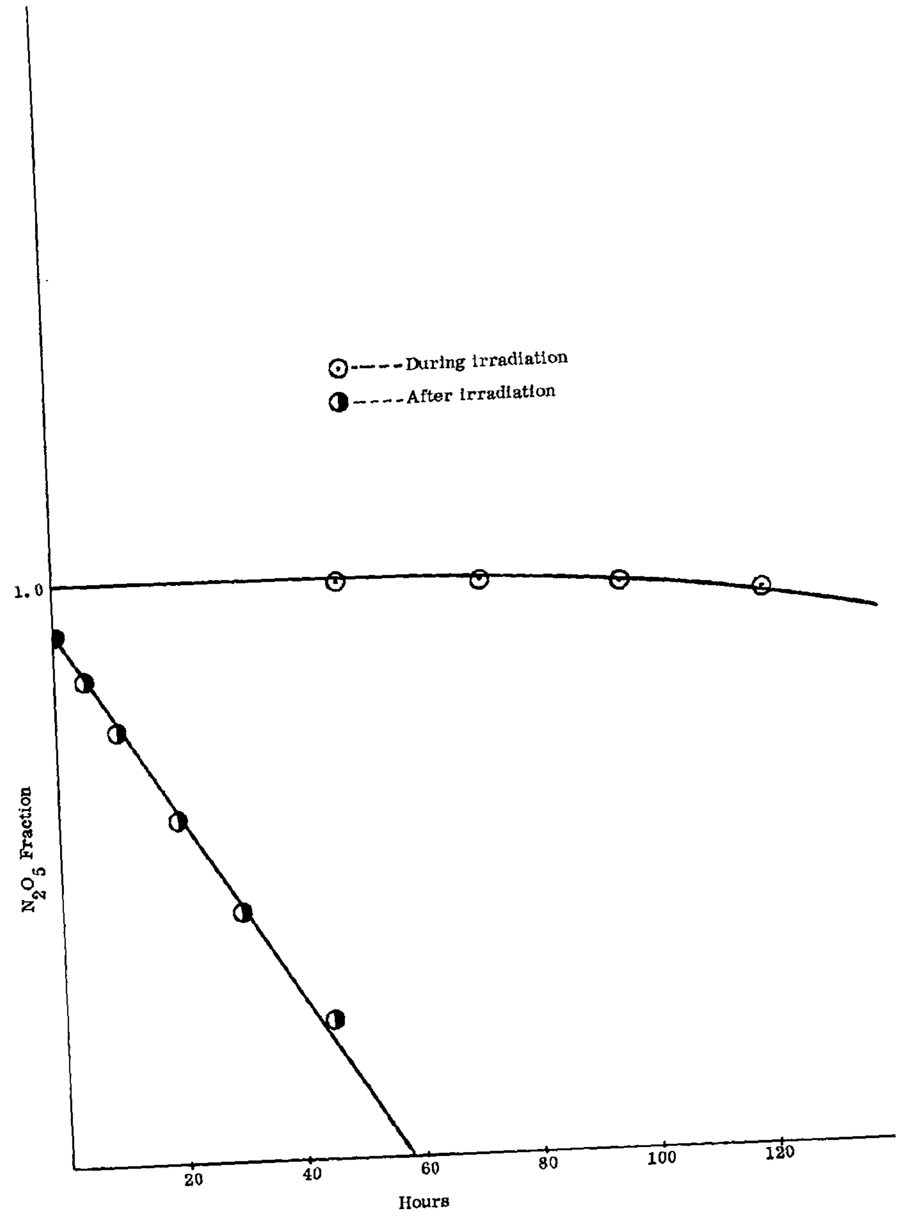

Figure 4. Relative Rates of N_2O_5 Decomposition During and After Irradiation at 20° C

Identification of N_2O

When the kinetics of decomposition of the thermally unstable product of radiolysis had been established, it became possible to investigate the existence of additional radiolytic products. A series of samples was irradiated 96 hours and thermally equilibrated for 7 days at 25° C. Control samples (i. e., unirradiated $(N_2O_4)_l$) were included in this determination as in all determinations made in this study. As soon as the equilibrated samples had been degassed at -196° C and analyzed for O_2 and N_2 contents in the usual manner, a second degassing was performed at -130° C. At this temperature, $(N_2O_4)_s$ has no vapor pressure; hence, any gas collected would be either N_2O or possibly CO_2 as a contaminant. The gas collected was analyzed mass spectrometrically and the spectrum of the mass peaks was compared to those of the CO_2 and N_2O standards (Table 10). The peak height intensity ratios of the mass to charge ratios of the various combinations of the fragmentation fractions were used to identify the unknown gas. The values given in Table 11 compare well with those of the N_2O standard. In addition, it should be emphasized that the spectrum of the unknown had a strong 30 peak but contained no trace of a 22 peak. According to the spectrum of the CO_2 standard, the following fragmentation takes place:

$$CO_2 \longrightarrow CO_2^{++} + CO^+ + O^+ + CO_2^+ \qquad (8)$$

While the spectrum of the CO_2 standard contains a 22 peak but no 30 peak, that of the N_2O standard has a strong 30 peak but no 22 peak. It was therefore concluded that, on the basis of the mass spectrometric data, the gas fractionated at -130° C was N_2O. This conclusion was further substantiated by the results obtained with the Beckman vapor phase chromatography unit using silica gel heated at 40° C as the absorbing medium. The retention times of the unknown and N_2O standard, shown in Figure 5, were identical.

With the identification of the stable gaseous products of radiolysis thus accomplished, the dependence of their formation on dose was determined. After radiolysis, samples were thermally equilibrated prior to analysis. Figure 6 shows this dependence to be linear from 15 to 60 megarads, with corresponding constant G values calculated from the slope of each linear portion of the curve. Apparent induction periods exist for oxygen and for nitrogen, but not for nitrous oxide. This implies that the mechanism of N_2O formation is independent of those of O_2 and N_2 formation.

TABLE 10

Mass Spectrometric (M/e) Fragmentation of N_2O and CO_2 Standards

Standard	M/e Species					
CO_2	$44/CO_2^+$	------	$28/CO^+$	$22/CO_2^{++}$	$16/O^+$	-----
N_2O	$44/N_2O^+$	$30/NO^+$	$28/N_2^+$	------	$16/O^+$	$14/N^+$

TABLE 11

Mass Spectrometric Analysis of Radiolytic Product Fractionated at -130°C

M/e Fractions	Intensity (Peak Height) Ratios of M/e Fractions				
	N_2O Standard[a]	Experimental Determinations			
		1	2	3	4
$30/28 = NO^+/N_2$	2.65	2.60	2.25	2.39	2.62
$30/14 = NO^+/N^+$	5.53	5.48	5.15	5.45	5.51
$14/16 = N^+/O^+$	2.34	2.37	2.34	2.22	2.32
$44/30 = N_2O^+/NO^+$	2.90	3.28	3.02	3.02	3.10

[a] Based on $N_2O \longrightarrow NO^+ + N_2^+ + O^+ + N^+ + N_2O^+$ mass spectrometric fragmentation

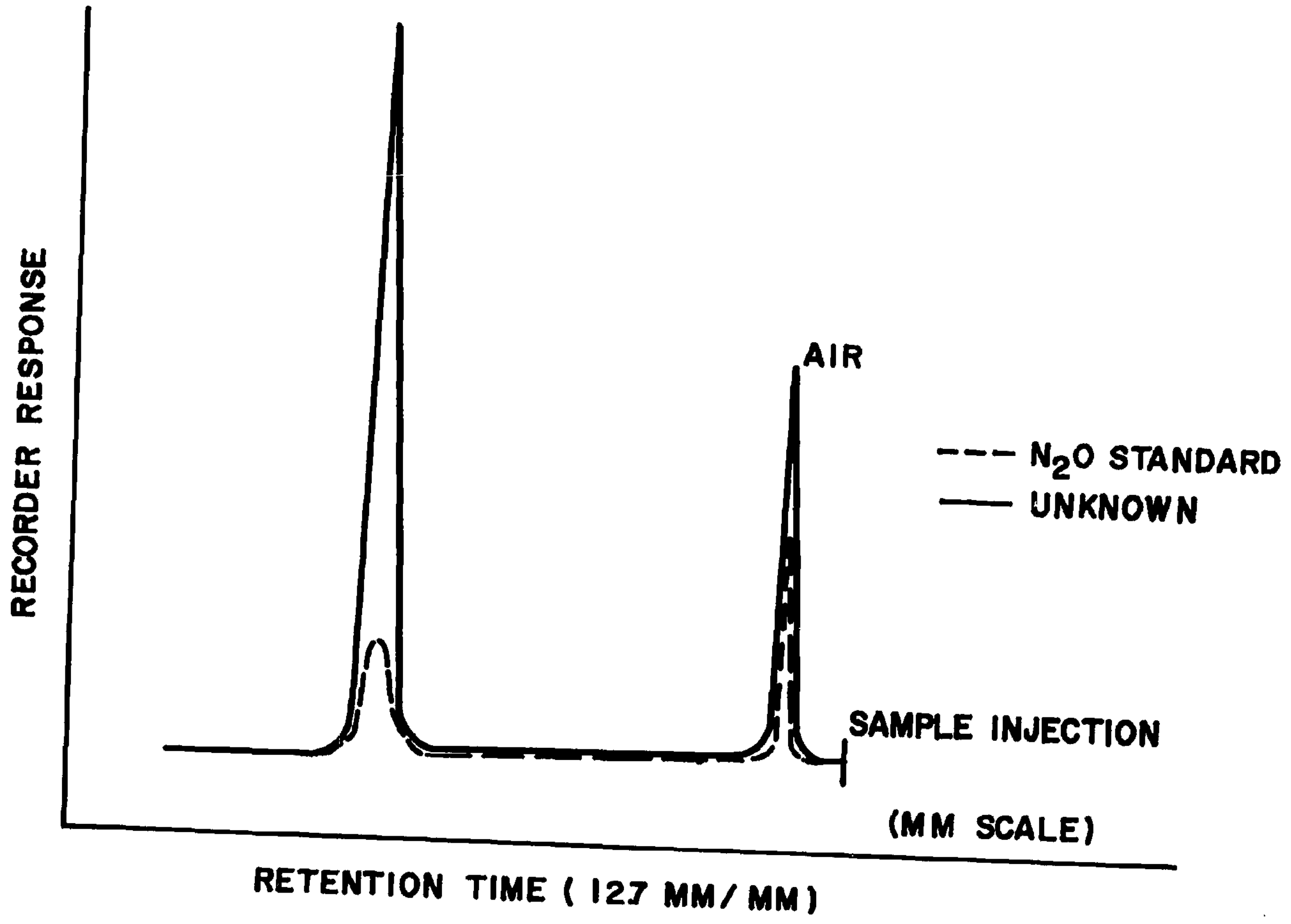

Figure 5. Vapor Phase Chromatogram Showing Relative Retention Times of Unknown and N_2O Standard

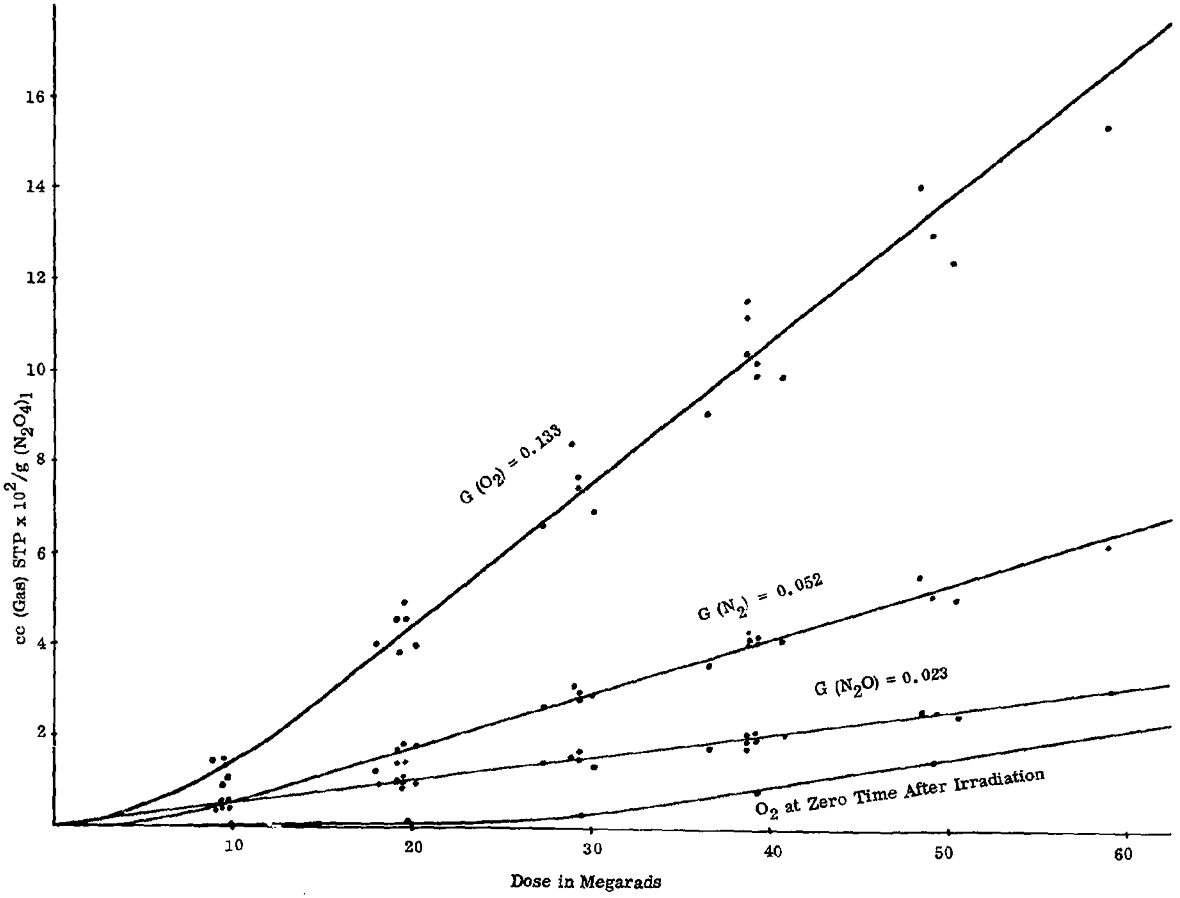

Figure 6. Cobalt-60 Gamma Radiolysis of Liquid N_2O_4 at 20°C. Dependence of Isolated Gaseous Products on Dose (Dose Rate 0.41 Mrad/hr)

Material Balance of Radiolytic Gaseous Products

Material balance calculations were based on the valence changes (i.e., changes in oxidation states) involved in the process of product formation according to the following equations:

$$N_2^{+4}O_4^{-2} \longrightarrow N_2^{\circ} + 2O_2^{\circ} \qquad (9)$$

$$2N_2^{+4}O_2^{-2} \longrightarrow 2N_2^{+1}O^{-2} + 3O_2^{\circ} \qquad (10)$$

For every N_2 formed, there is a gain of 4 electrons per atom of nitrogen. In the formation of N_2O, there is a gain of 3 electrons per atom of nitrogen, and no change in electrons for the bound oxygen. Finally, there is a loss of two electrons per atom of oxygen per O_2 produced. Multiplying the radiolytic yields of gaseous products by their respective valence changes,

$$4 \left[N_2\right] + 3 \left[N_2O\right] - 2 \left[O_2\right] = O \qquad (11)$$

or

$$2 \left[N_2\right] + 1.5 \left[N_2O\right] = \left[O_2\right] \qquad (12)$$

gives an evaluation of the material balance obtained experimentally. These values are listed in Table 12 and show an average oxygen deficiency of 2.3×10^{-7} mole O_2 per gram $(N_2O_4)_l$ or 2×10^{-5} mole O_2 per mole $(N_2O_4)_l$. The total observed decomposition of $(N_2O_4)_l$ based on

$$G(N_2O_4) = G(N_2) + G(N_2O) \qquad (13)$$

being $G(N_2O_4) = 0.052 + 0.023 = 0.075.$

Radiolysis of $(N_2O_4)_l$ Preparations, Including N_2 Sparging

It was considered possible that the oxygen used in the purification of $(N_2O_4)_l$, being entrained, was responsible for the formation of N_2O_5 during radiolysis. To check this, samples which had been sparged with N_2 after the usual sparging with O_2 were irradiated and studied for post-irradiation rate of oxygen evolution and dependence of product formation on dose in the manner as described in previous experiments. The amount of oxygen evolved at 20° ± 0.05° C was observed to increase with each successive sample analysis performed in time as shown in Table 13.

TABLE 12

Material Balance[a] of Isolated Gaseous Products of $(N_2O_4)_l$ Radiolysis

Expt. No	cc (Gas) STP x 10^2/g$(N_2O_4)_l$			$2N_2 + 1.5N_2O$ (A)	A - O_2	Dose Mr
	O_2	N_2	N_2O			
1-18-6	0.92	0.35	0.47	1.41	0.49	9.84
1-25-3	1.45	0.57	0.45	1.82	0.37	9.84
1-18-1	4.59	1.82	1.03	5.18	0.59	19.68
1-25-2	4.94	1.37	1.03	4.29	-0.65	19.68
1-18-2	7.70	2.91	1.62	8.25	0.55	29.52
1-25-1	7.50	2.83	1.62	8.09	0.39	29.52
11-30-4	9.87	4.08	2.00	11.16	1.29	40.70
1-18-3	10.25	4.04	2.11	11.25	1.00	39.36
1-18-5	9.90	4.12	1.90	11.09	1.19	39.36
1-18-4	12.96	5.04	2.50	12.96	0.87	49.20
12-14-4	12.42	4.95	2.42	13.52	1.10	50.45
1-25-4	15.34	6.11	2.96	16.66	1.32	59.04
7-4-5	11.55	4.38	1.70	11.31	-0.24	38.88
6-6-1	1.42	0.53	0.53	1.86	0.44	9.72
6-6-2	3.82	1.39	0.98	4.25	0.43	19.44
6-6-3	8.46	3.12	1.58	8.61	0.15	29,16
6-6-4	10.41	4.15	1.96	11.24	0.83	38.88
6-6-5	11.20	4.24	1.96	11.41	0.21	38.88
6-6-6	14.06	5.50	2.54	14.81	0.75	48.60
9-14-10	1.50	0.31	0.43	1.27	-0.23	9.17
9-14-8	4.00	1.20	0.91	3.77	-0.23	18.15
9-14-9	6.60	2.65	1.38	7.37	0.77	27.50
9-14-11	9.10	3.50	1.83	9.75	0.65	36.67
5-30-1	1.01	0.50	0.34	1.51	0.50	9.86
5-30-2	4.59	1.72	0.96	4.88	0.29	19.62
5-30-4	3.98	1.74	0.99	4.96	0.98	20.43
5-30-3	6.89	2.89	1.25	7.66	0.77	30.27
				Avg = 0.52		

[a] Based on $O_2 = 2N_2 + 1.5\ N_2O$

Mole O_2/gm$(N_2O_4)_l$ Deficiency $= \frac{5.2 \times 10^{-3}\ \text{cc/gm}N_2O_4 \times 10^{-3}\ \text{mole}}{22.4\ \text{cc/m Mole}} =$

2.3×10^{-7} or 2×10^{-5}/mole $(N_2O_4)_l$

TABLE 13

Post Irradiation Rate of N_2O_5 Decomposition at 20° C ± 0.05°

($(N_2O_4)_1$ purification included N_2 sparging)

Grams $(N_2O_4)_1$	mm Gas (N_2+O_2)	Percent O_2	°K	$\frac{\text{cc } (O_2) \text{ STP}}{\text{gm } (N_2O_4)_1}$ (x 10^2)	Fraction N_2O_5 Remaining	Seconds (x 10^{-4})	Spec. Rate Const. (x 10^4 sec^{-1})
5.800	113.7	38.9	295.2	2.80	0.758	0	—
5.780	161.0	56.9	296.0	5.83	0.518	2.88	0.13
5.690	182.5	62.4	297.0	7.31	0.395	5.76	0.11
5.730	195.8	64.1	296.5	8.01	0.306	8.64	0.10
5.581	207.2	66.6	295.0	9.98	0.136	17.46	0.10
5.632	244.0	72.5	294.5	11.55	0	$\rightarrow\infty$	—
							Average 0.11

The fractions of N_2O_5 corresponding to these amounts were used to calculate the specific rate constants. The average rate constant is in excellent agreement with those obtained from samples sparged with oxygen only. Figure 7 shows the curves for these comparable determinations to be superposable. Further comparisons of the effect of N_2 sparging with respect to the dependence of product formation on dose are shown in Figures 8 and 9. In all cases, the slopes of the curves are identical. These results indicate that the use of O_2 in purifying $(N_2O_4)_l$ is not in any way responsible for the formation of N_2O_5 during radiolysis.

Radiolysis of $(N_2O_4)_l/O_2$

On the basis of studies of the decomposition of N_2O_5 during and after radiation, it appeared that the oxygen given off in the radiolysis of $(N_2O_4)_l$ to N_2 and N_2O combines with N_2O_4 to form N_2O_5. During radiolysis, the N_2O_5 was shown to be stabilized in a gamma field. After radiolysis, however, it decomposes following the first order kinetics reported in the literature but at a slightly slower rate because of the prevailing dilution factor. These processes can be represented by the following set of equations:

$$5\ N_2O_4 \rightsquigarrow N_2 + 4\ N_2O_5 \qquad (14)$$

$$4\ N_2O_4 \rightsquigarrow N_2O + 3N_2O_5 \qquad (15)$$

$$N_2O_5 \overset{\longrightarrow}{\leftsquigarrow} N_2O_4 + 1/2O_2 \qquad (16)$$

and at thermal equilibrium,

$$2\ N_2O_5 \longrightarrow O_2 + 2\ N_2O_4 \qquad (17)$$

If this were indeed the mechanism of oxygen consumption and subsequent release after radiolysis, certainly any addition of oxygen to $(N_2O_4)_l$ would behave in the same manner. To establish the validity of this postulate, irradiation studies were conducted with known quantities of O_2 added to $(N_2O_4)_l$.

Double break seals, which facilitated the introduction of O_2 to $(N_2O_4)_l$ and subsequent degassing of products after radiolysis, were calibrated and the volume of gases was determined by the calculations shown in Table 14.

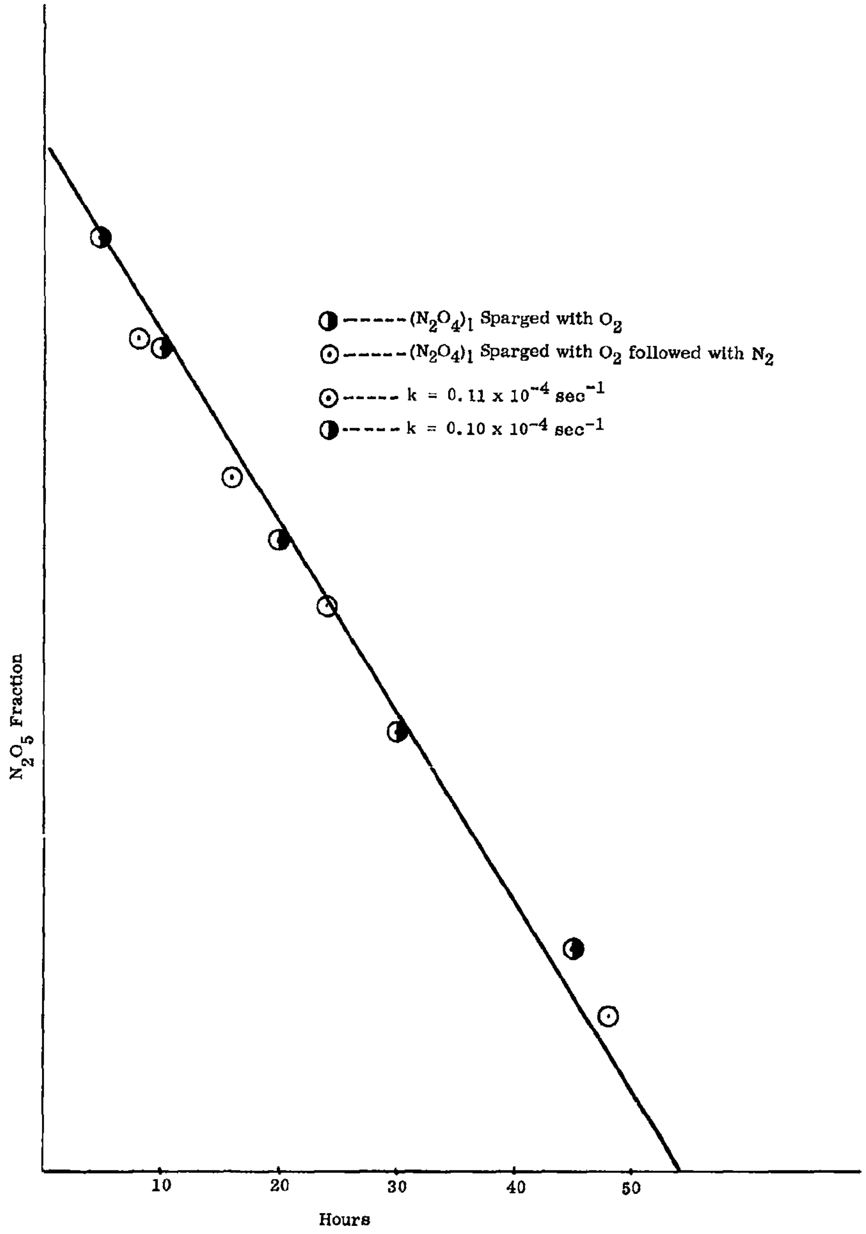

Figure 7. Dependence of Post Irradiation Rate of N_2O_5 Decomposition at 20° C On Variation in $(N_2O_4)_l$ Purification Procedure

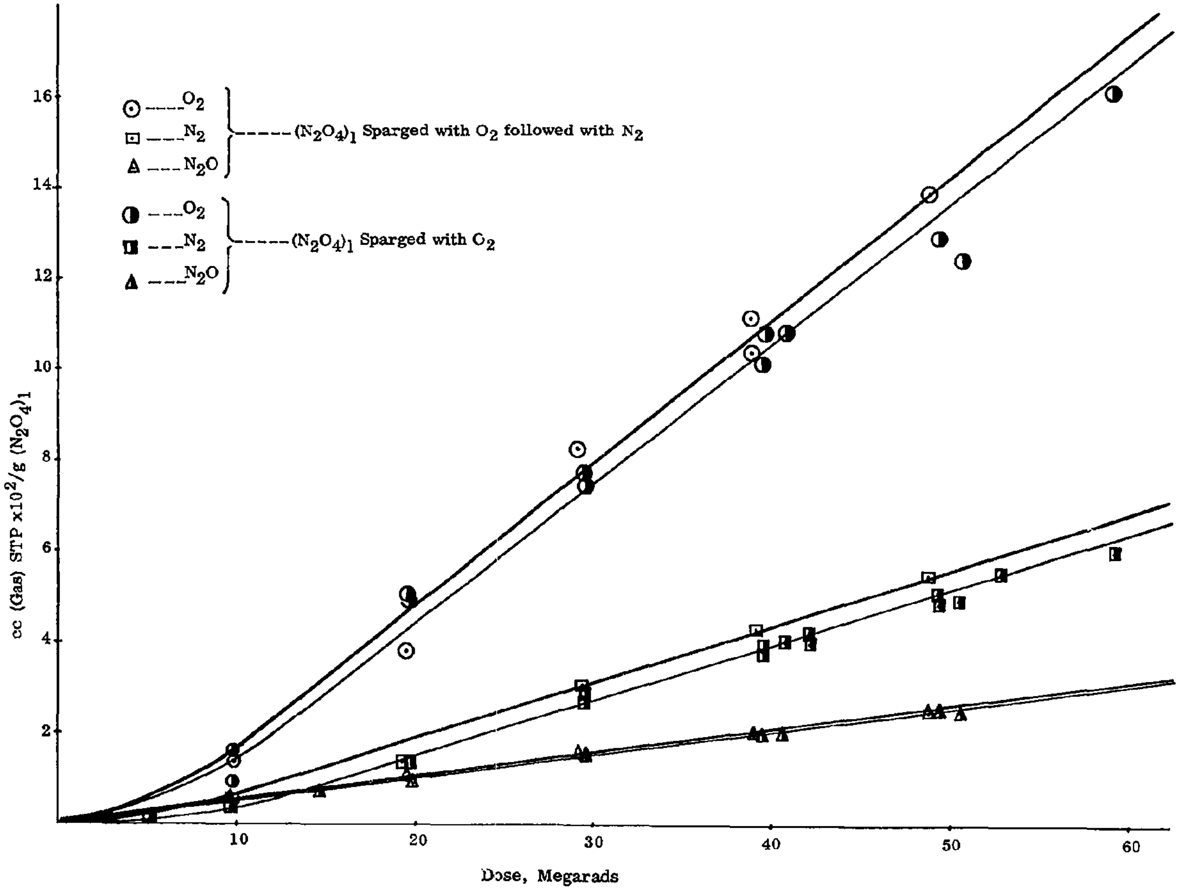

Figure 8. Effect of Variation in $(N_2O_4)_1$ Purification Procedure on Dependency of Yields of Products on Dose

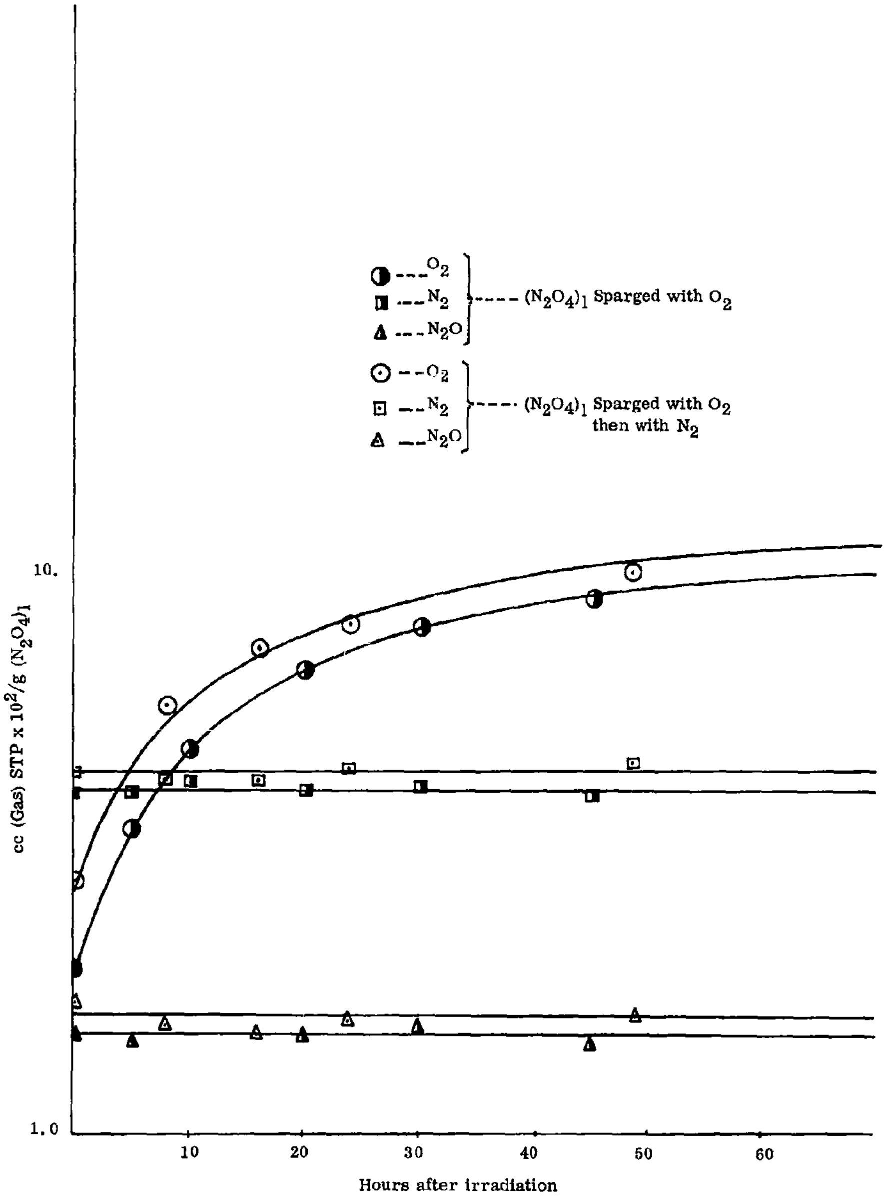

Figure 9. Dependence of Post Irradiation Rates of Gaseous Products Formation at 20°C On Variation in $(N_2O_4)_l$ Purification Procedure

TABLE 14

Quantities and Partial Pressures[b] of O_2 in Free Space Above $(N_2O_4)_l$ in Sealed Ampoules

Expt. No.	Break-Seal Vol (cc)[a] (V_1)	mm (O_2) Break-Seal Pres (P_1)	°K	cc (O_2) STP	Ampoule Vol. (cc)	Total Vol. (Amp. + V_1)	$(N_2O_4)_l$ Vol. (cc)	Free Space (V_2)	P.P. (O_2) Above $(N_2O_4)_l$ $P_1 \times V_1/V_2 = P_2$
8-31-3	1.666	546.0	295.2	1.106	3.46	5.13	2.82	2.31	394
8-31-11	1.887	518.0	294.5	1.192	4.45	6.34	3.53	2.81	348
8-31-10	1.853	518.0	294.5	1.170	4.18	6.03	3.29	2.74	350
8-31-12	1.826	546.0	295.2	1.215	4.23	6.06	3.21	2.85	350
9-7-5	1.792	304.5	293.7	0.668	4.43	6.22	3.63	2.59	210
9-7-1	1.813	304.0	295.5	0.670	4.53	6.34	3.48	2.86	193
9-7-3	1.847	304.5	295.4	0.684	4.26	6.11	3.84	2.27	248
9-7-2	1.905	304.0	295.5	0.706	4.28	6.19	3.22	2.97	196

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[a] Corrected for density of water at temperature determinations were made, viz; 0.99765g/cc at 22.5° C

[b] Uncorrected for solubility of O_2 in $(N_2O_4)_l$

The corresponding partial pressures of O_2 above the $(N_2O_4)_l$ are also included in Table 14. As a check on the technique of O_2 addition calculated quantities were compared to those obtained from analyses both in the presence and absence of $(N_2O_4)_l$. These results, given in Table 15, are shown to be in very good agreement. Directly after irradiation at various doses the samples were quenched in a dry-ice bath and analyzed in the usual manner for N_2, O_2, and N_2O content. This period of analyses was designated "zero time after irradiation." The samples were then resealed and analyzed for gaseous product formation after thermal equilibration (attained by storage at 25° C for 7 days). The gases isolated at zero time were N_2, O_2, and N_2O and, at thermal equilibrium, only O_2 was present, as is shown mass spectrometrically.

The relationship of these product analyses to the material balance calculations shown in Table 16 was based in part on Equation 12, which is derived from the valence changes involved in product formation. An equivalent method of arriving at this material balance formula is by use of Equations 14, 15, and 17, where the products at thermal equilibrium are equated to the total concentration of N_2O_5, i.e., $N_2 \sim 4\ N_2O_5$; $N_2O \sim 3\ N_2O_5$; and $O_2 \sim 2\ N_2O_5$. Therefore, the total concentration of N_2O_5 at thermal equilibrium (th. eq.) is given by

$$2\ (O_2)_{\text{th. eq.}} = (N_2O_5) = 4\ N_2 + 3\ N_2O \qquad (18)$$

However, to account for the oxygen added in these experiments, the quantity of O_2 determined at time zero, $(O_2)_t$, is subtracted from the quantity added initially, $(O_2)_o$, and the difference is added to Equation 18.

$$2\ (O_2)_{\text{th. eq.}} = (N_2O_5) = 4\ N_2 + 3\ N_2O + 2\left[(O_2)_o - (O_2)_t\right] \qquad (19)$$

or

$$(O_2)_{\text{th. eq.}} = (N_2O_5)/2 = 2\ N_2 + 1.5\ N_2O + \left[(O_2)_o - (O_2)_t\right] \qquad (20)$$

By the use of Equation 20, the material balance obtained in this set of experiments was found to be good to within ± 8%.

Plots of the volumes of N_2 and O_2 determined at zero time after irradiation and the volume of O_2 at thermal equilibrium versus dose in megarads are given in Figure 10. These determinations were made at partial pressures of O_2 ranging from 200 to 350 mm (see Table 21). The induction period for N_2 formation appears to have been eliminated

TABLE 15

Quantitative Determination of Gas Added to $(N_2C_4)_1$

	Calculated				Experimental		
Gas[a]	Break Seal Pres (mm)	°K	Break Seal Vol (cc)	cc (Gas) STP	mm (Gas)	°K	cc (Gas) STP
O_2	301.2	295.4	2.055	0.753	198	294.4	0.728
O_2	253.0	293.7	1.858	0.575	158	294.3	0.582
O_2	253.0	295.3	1.629	0.503	137	295,3	0.502
O_2	301.2	293.7	1.771	0.653	183	294.8	0.672
Ar	574.0	295.8	1.726	1.204	330	297.1	1.203
Ar	574.0	295.8	1.782	1.254	338	294.6	1.243
N_2[b]	375.5	295.4	1.743	0.796	220	297.0	0.802
N_2	375.5	295.4	1.737	0.793	219	296.5	0.800

[a] Gases scrubbed with activated charcoal in an appropriate refrigerant and mass spectrometric analyses showed their purity to be > 99%

[b] Determination made in the absence of $(N_2O_4)_1$

TABLE 16

Material Balance of Gaseous Products of $(N_2O_4)_l/O_2$ Radiolysis

Expt.[a] No.	$(N_2O_4)_l$ Wt. (grams)	P.P. (O_2) STP in Free Space (mm)	cc (O_2) STP Added Initially (C)	cc (Gas) STP At Zero Time After Irradn			cc (O_2) STP At Thermal Equilibrium[a] (E)	cc (Gas) STP/g $(N_2O_4)_l$			$2A+\frac{3}{2}B+C-D$	$\triangle$
				N_2 (A)	N_2O (B)	O_2 (D)		N_2	N_2O	O_2[b]	(X)	(E-X)
8-31-3	4.082	394	1.106	0.038	0.017	0.674	0.467	0.009	0.004	0.114	0.534	-0.067
8-31-11	5.100	348	1.192	0.094	0.044	0.842	0.608	0.018	0.009	0.119	0.604	0.004
8-31-10	4.780	350	1.170	0.132	0.070	0.938	0.614	0.028	0.015	0.129	0.601	0.013
8-31-12	4.650	350	1.215	0.185	0.088	1.097	0.618	0.040	0.019	0.133	0.620	-0.002
9-7-5	5.265	210	0.668	0.048	0.024	0.320	0.575	0.009	0.005	0.109	0.480	0.095
9-7-1	5.040	193	0.670	0.092	0.043	0.386	0.618	0.018	0.009	0.122	0.533	0.085
9-7-3	5.570	248	0.684	0.165	0.077	0.493	0.693	0.030	0.014	0.124	0.637	0.056
9-7-2	4.670	196	0.706	0.193	0.087	0.646	0.632	0.041	0.019	0.135	0.577	0.055

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[a] Source intensity 0.382 Mrad/hr.

[b] O_2 evolved after 7 days at 25° C

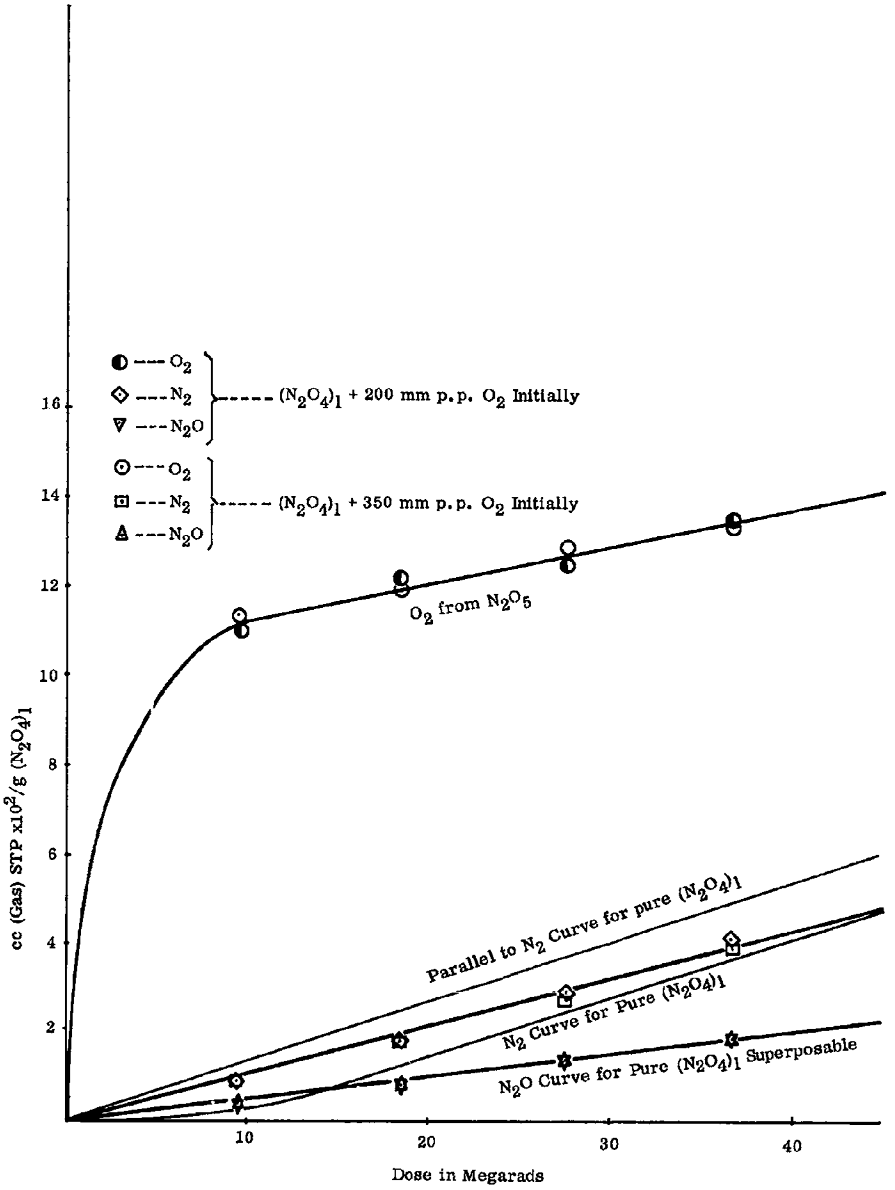


Figure 10. Cobalt-60 Gamma Radiolysis of Liquid N_2O_4 at 20°C. Effect of Adding Oxygen on Dependence of Gaseous Products Formation on Dose (Dose rate: 0.382 Mrad/hr)

by the addition of oxygen. This may indicate that O_2 is involved in the formation of N_2, increasing the concentration of precursors to their steady state proportions. Although the slope for N_2 is less, that of N_2O is superposable on the curves obtained for pure $(N_2O_4)_l$. Consistent with the premises made initially for this series of experiments, the rate of O_2 evolution is equivalent to the rate of N_2O_5 formation, which should be the same for the pure $(N_2O_4)_l$ as for the $(N_2O_4)_l$ containing O_2. From the slopes of the O_2 curves obtained in Figures 10 and 6, the latter including a curve for O_2 at zero time in the case of pure $(N_2O_4)_l$, the G (N_2O_5) formation corresponding to their respective rates of formation was calculated and found to be in excellent agreement.

$$G\,(N_2O_5)_{\text{pure }(N_2O_4)_l} = 1.11 \text{ and } G(N_2O_5)_{(N_2O_4)_l + O_2} = 1.12$$

(The calculations are given in the appendix of this report.) This, then, unequivocally establishes the formation of N_2O_5 via the combination with the oxygen present, whether added initially or, as a product of radiolysis, formed during irradiation.

Radiolysis of $(N_2O_4)_l/Ar$

The noble gases are often added to systems under investigation in radiation studies for the more efficient absorption of photon energy via a charge-transfer mechanism. The inert gases act as energy sinks, as do catalysts, effectively transferring the incident energy to the system being radiolyzed. To investigate this effect, known quantities of argon were added to $(N_2O_4)_l$ in the manner outlined for the O_2 additions, subjected to various doses, and analyzed for product formation. The gases isolated at thermal equilibrium were the same and in identical proportions as those obtained from the radiolysis of pure $(N_2O_4)_l$. These results, summarized in Figure 11, show the dependence of product formation on dose for all three gases to be linear from 15 to 40 megarads, with slopes superposable on those obtained for pure $(N_2O_4)_l$. The fact that the presence of argon had no effect on the yields of the products of radiolysis can be attributed to the apparent insolubility of argon in $(N_2O_4)_l$.

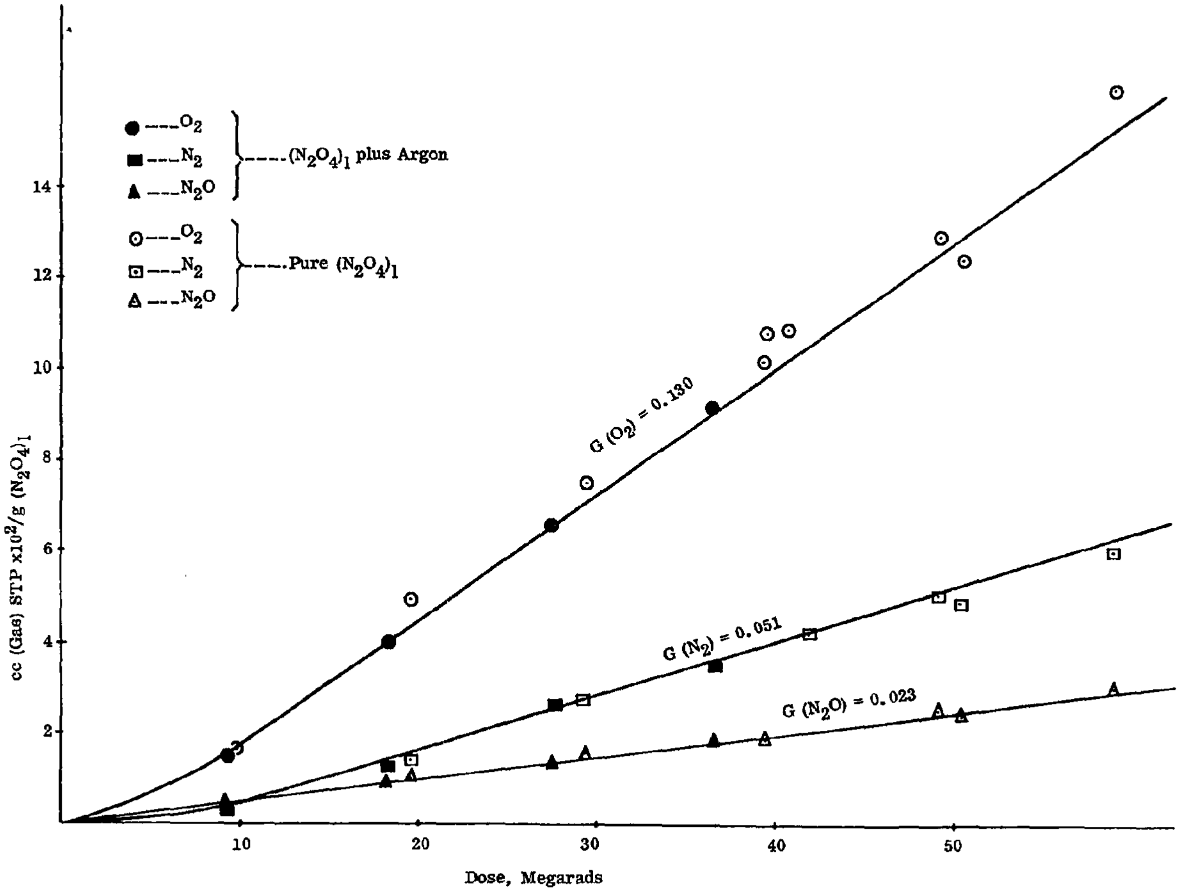


Figure 11. Effect of Argon on Dependence of Yields of Products on Dose

Effect of Dose Rate on Radiolysis of $(N_2O_4)_1$

The dependence of product formation on the intensity of a gamma field is given by the following relationships:

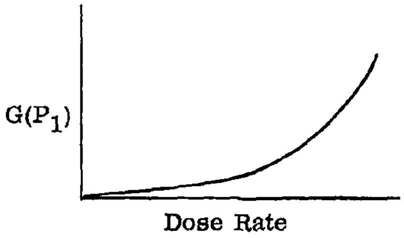
$$\text{Let } R\cdot + R\cdot \xrightarrow{k_1} P_1 \tag{21}$$

$$R\cdot + S \xrightarrow{k_2} P_2 \tag{22}$$

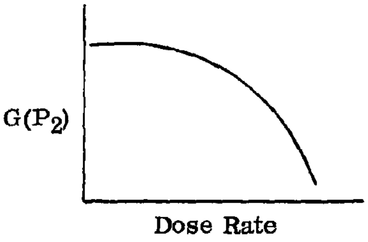
where S = molecule; R · = radical.
Then,

$$\frac{k_1(R\cdot)}{k_2(S)} = \frac{k_1(R\cdot)^2}{k_2(S)(R)} \tag{23}$$

It is seen from Equation 23 that the rate of radical-radical combination is dependent on the square of the concentration. Since the concentration of such reactive species is a function of source intensity, processes involving competing R· + R· and R· + S combinations would be affected by variations in intensities of incident radiations. This effect would result in the following types of curves:

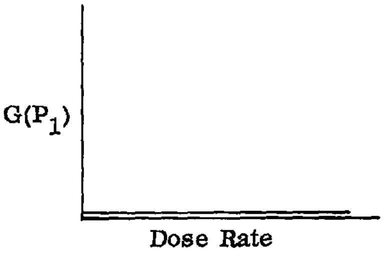


I

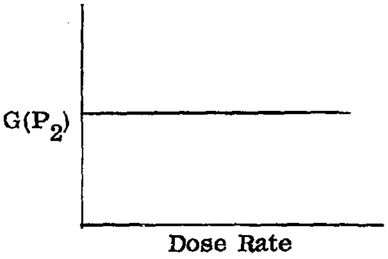


II

For those events involving only R· + S but no R· + R· reactions, the expected curves would be:



III



IV

To determine the effect of the intensity of radiation on the formation of products, samples were irradiated with a cobalt-60 source having one-thirtieth the intensity of the source normally used in this study. Samples were irradiated as a function of dose, and analyzed for product formation after thermal equilibration. Figure 12 shows that the radiation dose has no effect on product formation, since the curves obtained are superposable on those derived from irradiations with the normally more intense source. When G values calculated from the linear portions of these curves are plotted against dose rate, it is obvious that the resulting curve will be type IV. This indicates that the processes taking place during irradiation are not of the radical-radical type but rather of the radical-molecule type. With establishment of the independence of product formation in relation to changes in the intensity of incident radiation, it became possible to study the induction period more accurately using a low intensity source. Figure 13 shows the induction part of the curve to be real in that straight lines for O_2 and N_2 formation could not possibly be drawn through the origin but must intercept the X axis. At the same time the linear curve for N_2O is equally established as passing through the origin and found to be independent of source strength.

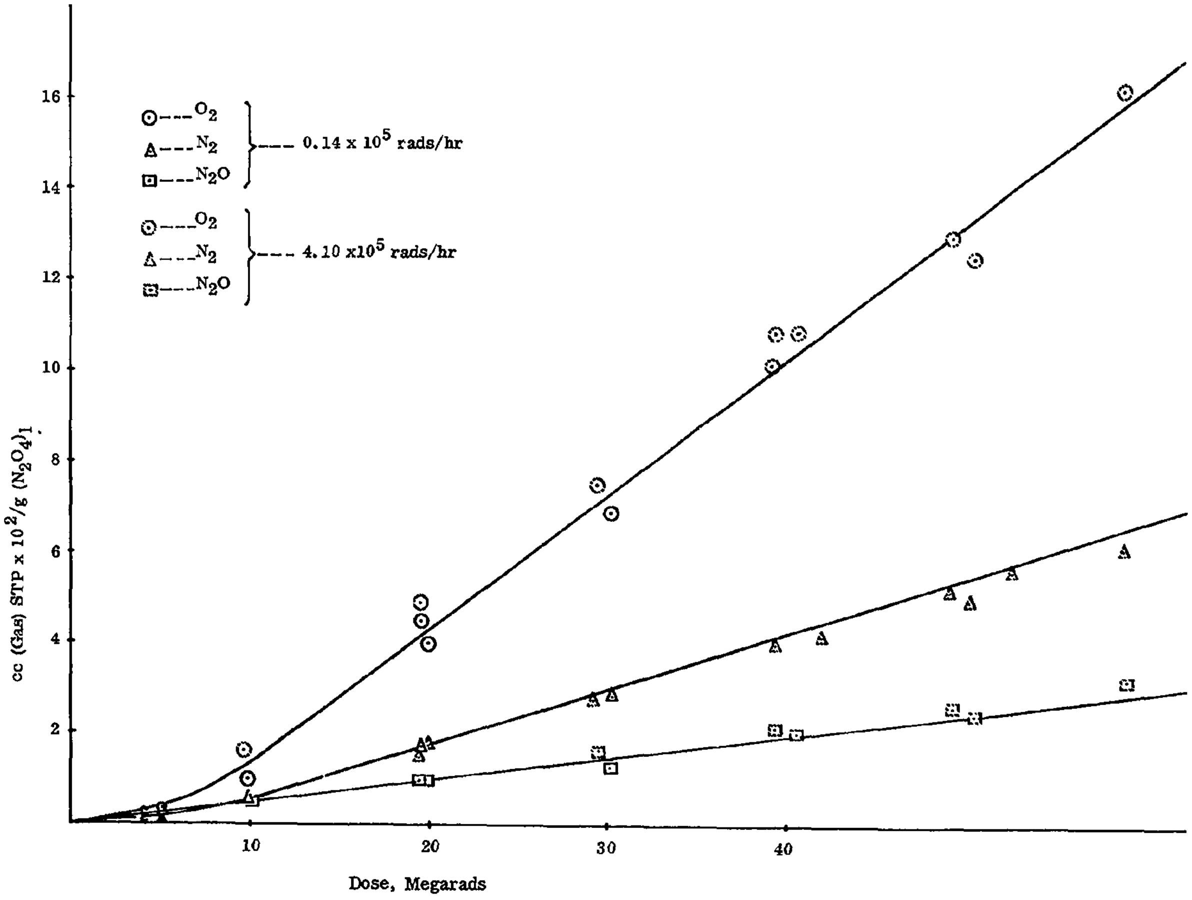


Figure 12 Dependence of Gaseous Products Formation During Radiolysis on Dose at Different Rates

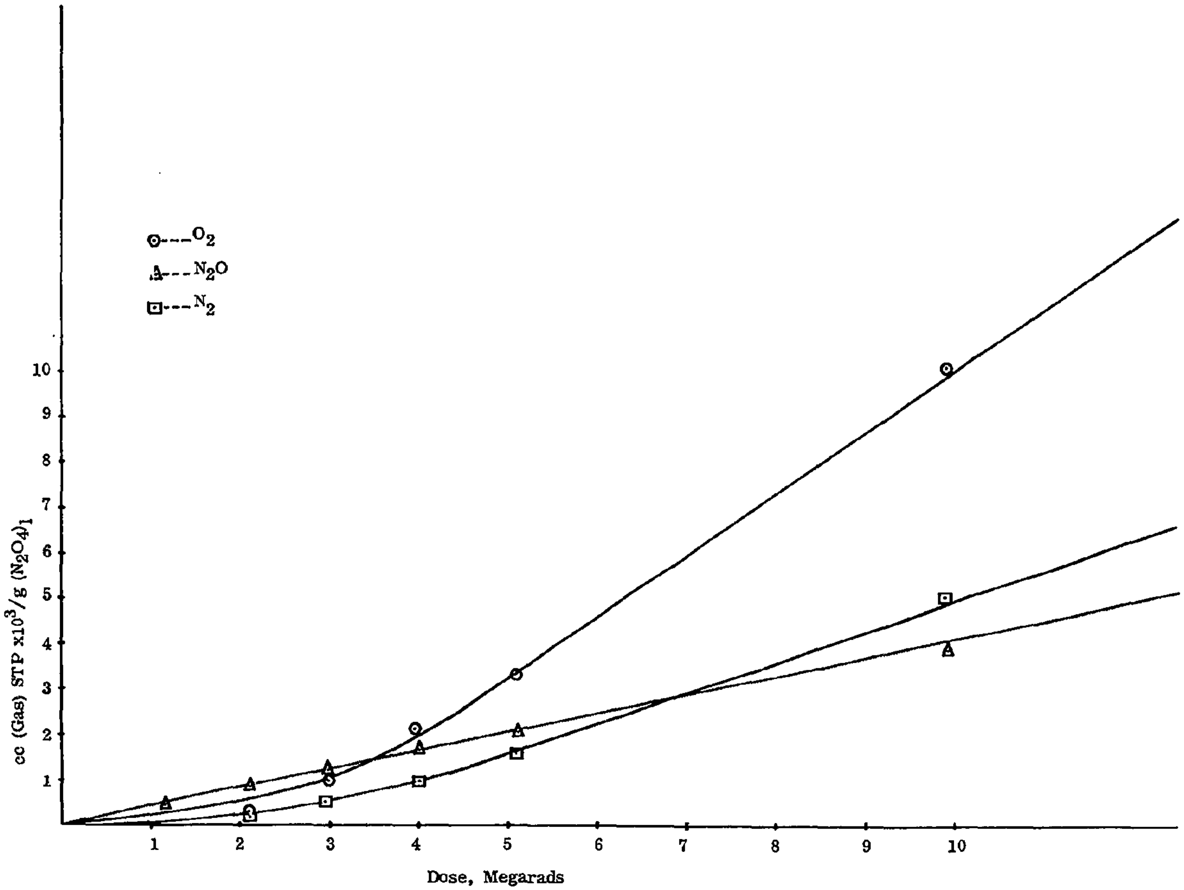


Figure 13. Cobalt-60 Radiolysis of $(N_2O_4)_l$ at 20° C; Dependence of G (O_2), G (N_2), and G (N_2) on Dose (Source Intensity 1.37 x 10^4r/hr)

EXPERIMENTAL PROCEDURES

Purification of $(N_2O_4)_1$

Tank gas (99% pure) was liquefied in approximately 40 cc aliquots and sparged with oxygen purified by passage over hot CuO and through a dry-ice trap. The $(N_2O_4)_1$ was distilled twice through phosphorus pentoxide-saturated glass wool and degassed two times at -78° C. (The glass wool used in this manner was treated with mixed HNO_3/H_2SO_4 acids and washed repeatedly with boiling distilled water until neutral to blue litmus and dried several days in an oven set at 110° C.) The $(N_2O_4)_1$ was then transferred to that part of the vacuum line protected from grease by glass bead traps and degassed a third time at -78° C. Only the center cut was distilled into 5 cc pyrex break seals for irradiation studies. Kel-F grease (chlorotrifluoropolyethylene) which was found to be inert to NO_2 was used on all standard joints and stopcocks. (See Figure 14 for details of apparatus.)

Gas Analyses

After radiolysis, the samples were degassed at -196° C and the N_2/O_2 gas mixture was toeplered into the McLeod gauge end of the vacuum line. The total quantity of gas was determined in the manner usually employed in vacuum techniques. Aliquots were reserved for mass spectrometric check analyses and the remainder was analyzed by the platinum filament combustion method. Approximately 5 microns of the unknown mixture was used for each determination, designated P_I. An estimated excess of H_2 (Purified and checked mass spectrometrically to have a purity of better than 99%) equivalent to P_I assumed to be 100% O_2 was added to P_I and the total pressure denoted as P_T. The platinum filament was then heated to the barely perceptible glow point and the water of combustion was removed by means of a cold finger at -196° C. The combustion was considered complete when pressure readings became constant. The residual gas pressure at the end of combustion was termed P_R. Then,

$$\frac{P_T - P_R}{3P_I} \times 100 = \%O_2.$$

Mass spectrometric check analyses of N_2/O_2 were calculated from the relative mass peak heights and corrected for the respective peak height sensitivity response differences of the recording instrument, e.g.,

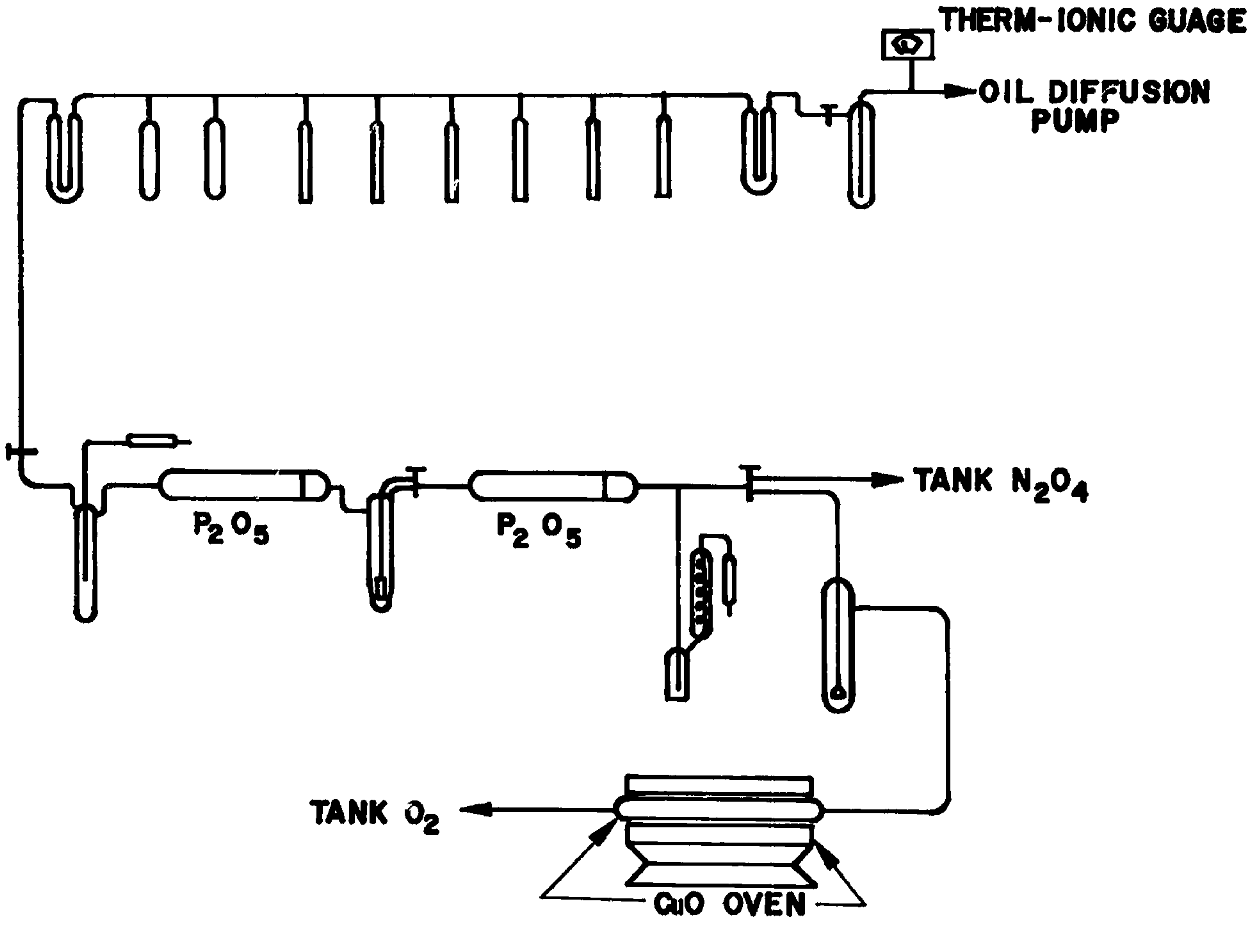


Figure 14 Apparatus for $(N_2O_4)_1$ Purification and Sample Preparation

sensitivity for O_2 = 344.2 divisions of peak height per mm pressure and 395.0 divisions per mm pressure for N_2. (See Figure 15 for details of apparatus.)

N_2O was isolated at -130° C using a 2-chlorobutane-liquid nitrogen bath directly after degassing irradiated samples at -196° C. The gas was then transferred to a cold finger and degassed at -196° C prior to final pressure readings. N_2O was identified mass spectrometrically and checked by vapor phase chromatographic analysis using standard reference samples in each method of analysis. A GC-2 instrument equipped with a 4-foot silica gel (70010) column heated to 40° C was used in the check analysis.

Preparation of Synthetic Solutions of N_2O_5 in $(N_2O_4)_l$

$(N_2O_4)_l$ purified in the manner outlined above was transferred under vacuum to a specially designed bubbler adaptable to a commercially available ozonizer apparatus. Before exposing the $(N_2O_4)_l$ to atmospheric pressure the entire glassware apparatus of the ozonizer was flushed with dry oxygen. The oxygen was dried by passage through a P_2O_5 tube, followed by a dry-ice trap. The outlet to the atmosphere was affixed with a drying tube filled with Drierite. After flushing for five minutes, the ozonizer was turned on and the $(N_2O_4)_l$ sparged with the O_3/O_2 mixture at a gentle fixed rate for 10 minutes. To minimize the loss of N_2O_4, the bubbler containing the $(N_2O_4)_l$ was immersed in a brine-ice bath. The solution of N_2O_5 in $(N_2O_4)_l$ was then attached to the vacuum line and degassed twice at -78° C and transferred to a set of six break-seal ampoules radially connected to a common tubing. The entire set of ampoules was immersed in a common dry-ice bath. By this arrangement, the ampoules were simultaneously and uniformly filled. Prior to flame sealing, the solutions were degassed a third time.

Oxygen and Argon Additions

A double break-seal of the type shown below was used for the addition of known quantities of oxygen and argon.

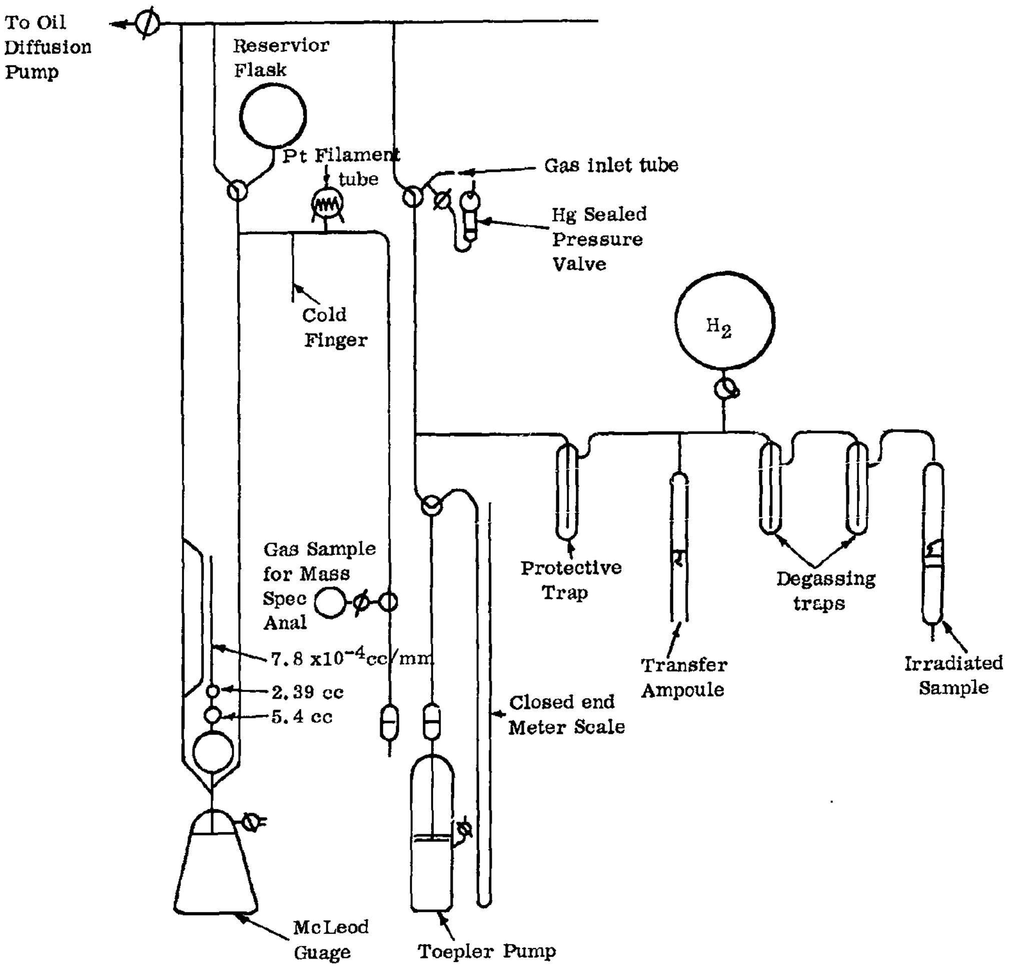
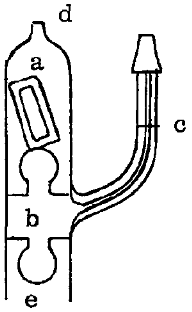


Figure 15. Vacuum Line for Gas Analyses



Volume b was calibrated by filling it to point c with water devoid of air bubbles. This was accomplished with a syringe affixed to a flexible stainless steel capillary tube inserted through the one millimeter bore side arm. The double break seal was attached to the vacuum line and either pure oxygen or argon (analyzed mass spectrometrically for purity) was introduced at pressures read on the meter scale. Using a small sharp flame, the side arm was rapidly sealed at the calibration line. Obtaining the volumes and pressures in this manner, the quantity of gas in the double break seal was accurately determined. The ampoule containing the glass encased hammer and a known quantity of gas was then attached to the sample preparation line. Pure $(N_2O_4)_1$ was distilled into "a" in the manner described above and flame-sealed at "d". The end of the break seal in contact with the hammer was broken, allowing the gas to intermix with $(N_2O_4)_1$. After radiolysis, a second glass-encased hammer was inserted through end "e". The ampoule was then placed on the vacuum line (with "e" end up) and analyzed as usual.

CONCLUSIONS

The products of cobalt-60 gamma radiolysis of liquid N_2O_4 have been found to be N_2, N_2O, and N_2O_5. The processes involved in these product formations are of the radical-molecule type. After radiolysis, the oxygen evolved at thermal equilibrium, due to the decomposition of N_2O_5 following first order kinetics, is in material balance with two parts of N_2 to one of N_2O. The net mode of product formation has been shown to include the following steps and stoichiometric proportions:

$$2N_2O_4 \rightsquigarrow 2N_2 + 4O_2 \qquad (1)$$

$$8N_2O_4 + 4O_2 \rightsquigarrow 8N_2O_5 \qquad (2)$$

$$N_2O_4 \rightsquigarrow N_2O + \frac{3}{2}\ O_2 \qquad (3)$$

$$3N_2O_4 + \frac{3}{2}\ O_2 \rightsquigarrow 3N_2O_5 \qquad (4)$$

Addition of Equations 1 - 4 gives us

$$14N_2O_4 \rightsquigarrow 2N_2 + N_2O + 11N_2O_5 \qquad (5)$$

Then, at thermal equilibrium,

$$11N_2O_5 \longrightarrow 11N_2O_4 + 5\frac{1}{2}\ O_2 \qquad (6)$$

Subtracting (6) from (5) gives

$$3N_2O_4 \longrightarrow 2N_2 + N_2O + 5\frac{1}{2}\ O_2 \qquad (7)$$

Initially, the radiation-induced reactions produce O_2 or N_2O_5, N_2O, and some precursor of N_2. The precursor is then converted to N_2 by a process dependent on dose and therefore not thermally spontaneous. This is based on the experimental data showing the N_2 buildup to be independent of dose rate and temperature. This means that during the induction period for N_2, in the 10-20 Mrad range, the precursor is stable in solution for 24 hours. The concentration of the precursor would be given by the negative intercept of the N_2 curve, obtained from Figure 6, i.e.,

$$\frac{6.25 \times 10^{-3}\ cc(N_2)/g(N_2O_4)}{2.24 \times 10^{4}\ cc/mole} = 2.9 \times 10^{-7}\ mole/g(N_2O_4)$$

or 2.9×10^{-5} mole of precursor/mole N_2O_4

When O_2 is added, there is no intercept and it is therefore concluded that the excess O_2 reacts with the precursor or an intermediate of the precursor to produce N_2. It must be emphasized that this reaction takes place only in the presence of an excess of O_2.

A possible mechanism for N_2 production could be based on the formation of N_2O_3 as the precursor, viz.

$$N_2O_4 \rightsquigarrow N_2O_3 + O \qquad \text{or} \tag{8}$$

$$N_2O_4 \rightsquigarrow NO + NO_2 + O \tag{9}$$

where $N_2O_3 \rightleftarrows NO + NO_2$

Since the ionization potential of NO is less than that of NO_2,

$$NO \rightsquigarrow NO^+ + e \tag{10}$$

and the charge is then transferred via

$$NO^+ + e \rightsquigarrow N + O. \tag{11}$$

Finally,

$$N + NO_2 \rightsquigarrow N_2 + O_2. \tag{12}$$

In the presence of an excess of O_2, the reaction given in (9) is followed by,

$$NO_2 + xs(O) \rightsquigarrow NO + O_2 \tag{13}$$

In this manner, the steady state concentration of N_2O_3 or ($NO + NO_2$) is attained instantaneously, and hence there is no induction period.

The extent to which these radical-molecule processes proceed to stable product formation has been shown to be in the order of 0.1 to

0.01 milli molar concentrations. Since the number of molecules of N_2O_4 decomposing per 100 electron volts absorbed is only 0.075, it is quite obvious that $(N_2O_4)_l$ is relatively radiation resistant. In more practical terms, this means that $(N_2O_4)_l$ must receive a total dose in the tens of million rads, in order to produce 0.001 mole percent decomposition. To the missile scientist, this amply signifies that $(N_2O_4)_l$, as a powerful oxidant, would be stable by itself in fields of ionizing radiation, such as the van Allen belt and in solar flare drifts.

To the preparative radiation chemist, low G values mean that the velocity of the reverse reaction is greater than that of the forward reaction induced by radiation. Under such steady-state conditions reactive intermediates such as N_2O_5, NO_2^+, and NO_2^* have prolonged half-lives in an ionizing field, thereby favoring the formation of reaction products with added constituents. When constituents such as benzene are added in small concentrations, relative to the $(N_2O_4)_l$, they would be expected to behave as scavengers and combine with most of the reactive intermediates. Opportunities for product formation could be considered multiple and promising with respect to types of products isolated. This would therefore serve as an indication of the variety of reactions possible under such conditions. Certainly, N_2O_5 as a product of radiolysis, stabilized in a gamma field, should prove to be most conducive to the formation of products of interest in Ordnance chemistry.

RECOMMENDATIONS

The results obtained in this initial study of the radiation chemistry of $(N_2O_4)_l$ serve as a basis for optimizing conditions for product formation from the radiolysis of $(N_2O_4)_l$ with added constituents. This work should therefore be continued in its second phase to include the isolation and identification of reaction products resulting from the scavenging of the multiple reactive intermediate species indicated herein.

In passing to this second phase of investigation, to more completely establish the proposed mechanism, the effect of NO on the radiolysis of $(N_2O_4)_l$ should also be studied. The addition of NO to $(N_2O_4)_l$ would be expected to have a decided effect on product formation since it appears that N_2O_3 or its equivalent NO must play an important role in the mechanism of $(N_2O_4)_l$ radiolysis (See Equations 9-13 in "Conclusions").

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APPENDIX

Sample Calculations

Oxygen Analysis, Platinum Filament Combustion Method.

The formula, $\frac{P_T - P_R}{3 P_I} \times 100 = \%O_2$, used in this analysis is based on the relationship given by the equation:

$$[N_2 + O_2] + 2 H_2 \longrightarrow N_2 + 2 H_2 O \downarrow -196° C$$

where P_I = mm Hg ($N_2 + O_2$)

P_T = mm Hg ($N_2 + O_2 + H_2$ in xs)

P_R = mm Hg (N_2 + xs H_2),

and one-third of the volume of gas contraction, ($P_I - P_R$), is equivalent to the oxygen content in the gas mixture. This quantity of oxygen, represented by ($P_T - P_R$)x0.333 over the O_2/N_2 mixture, P_I, gives the fraction of oxygen. For an actual determination, the pressure reading in the capillary of the McLeod gage is squared, viz., mm Hg x mm capillary length = $(mm)^2$ Hg-capillary length. Since the quantity, 7.8×10^{-4} cc per mm capillary length is a constant multiple factor, it was eliminated and the resultant values in units of $(mm)^2$ Hg in the fraction of pressure readings then cancelled out.

Specific Gas Volume Determinations [cc (Gas) STP/g $(N_2O_4)_1$]

These determinations were made by using the following formula:

$$\frac{1.262 \times P' \times F \times V \times T°}{g \text{ Wt } (N_2O_4)_1 \times T' \times P°} = \frac{\text{cc (Gas) STP}}{g\ (N_2O_4)_1} = Vs$$

where 1.262 = factor giving total volume of gas collected

T° = 273° K; T' = observed °K

P° = 760 mm

P' = mm Hg ($N_2 + O_2$) gas fractionated at -196° C
or mm Hg (N_2O) gas fractionated at -130° C

F = O_2 or N_2 fraction
or 1.0 in the case of N_2O

V = calibrated volumes, 2.39 or 5.40 cc

For very small V, when pressure readings are taken from the capillary section of the McLeod gage

$P' = P^2 = [\text{mm Hg x mm capillary length}]\ (N_2 + O_2)$ or (N_2O), and

$V = V' = 7.8 \times 10^{-4}$ cc/mm capillary length.

G-Value Calculations

The following formula was used in calculating G values:

$$G = \frac{V \times v}{W \times T \times R \times r(f)} = \frac{\text{no. molecules}}{100 \text{ ev absorbed}}$$

where: V = number of cc at STP

$v = 2.688 \times 10^{19}$ molecules / (cc) STP

W = weight of sample in grams

T = time of irradiation (usually in hours)

R = dose rate in rads/hour

$r = 6.24 \times 10^{13}$ ev absorbed / weight of sample in grams

f = correction factor for electron density differences*

*For the irradiation of a given system, the total number of electron volts (ev) absorbed by way of Compton interaction is dependent on electron density per unit weight and source intensity. Source intensity is measured with a Fricke dosimeter, consisting of an aqueous solution of ferrous sulfate in 0.8N H_2SO_4. The calculated total dose absorbed must therefore be corrected for the difference between the electron density of the liquid N_2O_4 and that of the dosimeter solution (per unit-weight). This correction factor, designated "f", is determined as follows:

Density of 0.8N H_2SO_4 = 1.0229, or wt (1l soln) = 1022.9g

Equivalent weight of 0.8N H_2SO_4 = 39.2g, or 0.4 moles H_2SO_4

Weight of water = 1022.9 - 39.2 = 983.7g, or 54.65 moles H_2O

Number of electrons / molecule H_2O = 10

Number of electrons / molecule H_2SO_4 = 50

Therefore, total number of electrons / 0.8N H_2SO_4 = (54.65 x 10) + (0.4 x 50) = 566.5. Number of electrons / g 0.8N H_2SO_4 = 566.5 / 1022.9 = 0.554

1 liter N_2O_4 weighs 1447.0 g; number moles = 1447/92 = 15.74/l

Number of electrons per molecule N_2O_4 = 46

Total number of electrons per liter = 15.74 x 46 = 724 e's/l

Number of electrons / g N_2O_4 $= \frac{724\text{ e's/l}}{1447\text{g/l}} = 0.5$

Therefore f = 0.5/0.554.

An alternate method of calculating the G value is from the slope of the curve in terms of cc(gas)STP/g $(N_2O_4)_l$ on the ordinate rise over the corresponding dose increment on the abscissa, i.e.,

$$\frac{Vs}{D} = \text{slope}$$

where Vs = specific gas volume = cc(gas)STP/g sample wt = $\frac{V}{W}$

and D = total dose = $T \times R$

then $$\frac{Vs}{D} \times \frac{v}{r(f)} = G$$

Calculation of G (N_2O_5) Formation from Irradiated $(N_2O_4)_l$ With and Without Oxygen Added.

The G (N_2O_5) formation was calculated by the use of:

$$\frac{Vs}{D} \times \frac{v}{r} = G$$

where Vs is the specific volume of oxygen, and the rate of oxygen build-up given by Vs/D is equivalent to the rate of N_2O_5 formation.

$(N_2O_4)_1$ plus O_2

The rate of N_2O_5 formation was obtained from the slope of the oxygen curve in Figure 10, viz.,

$$\frac{1.7 \times 10^{-2} \text{ cc } (O_2)/g}{20 \text{ Mrad}} = 8.5 \times 10^{-4} \ \frac{\text{cc } (O_2)}{g - \text{Mrad}}$$

Multiplying this value by the dose rate gives the rate of N_2O_5 build-up in cc (O_2)/g-hr, i.e.,

$$8.5 \times 10^{-4} \text{ cc } (O_2)/_{g\text{-Mrad}} \times 0.382 \text{ Mrad/hr} = 3.25 \times 10^{-4} \text{ cc } (O_2)/\text{g-hr}$$

This rate of N_2O_5 formation must be corrected by adding to it the rate of formation represented by the rate of N_2O_5 decomposition after irradiation, viz., 1.0×10^{-5} sec^{-1} or
1.0×10^{5} 1/sec $\times$ 3.6×10^{3} sec/hr = 3.6×10^{-2} hr^{-1}
multiplied by the decomposition rate concentration, 0.125cc (O_2)/g (taken from the mean of the curve in Figure 10), i.e.,
3.6×10^{-2} hr^{-1} $\times$ 0.125 cc (O_2)/g = 4.5×10^{-3} cc (O_2)/g-hr

The total N_2O_5 buildup rate in terms of O_2 is therefore:

$$0.325 \times 10^{-3} \text{cc } (O_2)/\text{g-hr} + 4.50 \times 10^{-3} \text{ cc } (O_2)/\text{g-hr} =$$

$$4.825 \times 10^{-3} \text{ cc } (O_2)/\text{g-hr}$$

Dividing by the dose rate, the corrected rate of O_2 uptake or N_2O_5 formation is obtained in terms of cc (O_2)/g-Mrad, i.e.,

$$4.825 \times 10^{-3} \text{ cc/g-hr} \times \text{hr}/0.382 \text{ Mrad} = 1.26 \times 10^{-2} \text{ cc } (O_2)/\text{g-Mrad}$$

However, since the number of moles of N_2O_5 equals twice the number of moles of O_2, the $G(N_2O_5)$ formation is given by

$$G(N_2O_5) = \frac{2 \times 1.26 \times 10^{-2} \text{ cc } (O_2)/_{\text{Mrad}} \times 6.02 \times 10^{23} \text{ molecules}/_{\text{mole}}}{2.24 \times 10^{4} \text{ cc } (O_2)/_{\text{mole}} \times 6.24 \times 10^{17} \text{ ev}/_{\text{Mrad}\cdot 100 \text{ ev}}} = 1.12$$

Pure $(N_2O_4)_1$:

The net rate of N_2O_5 formation, in terms of cc $(O_2)_n$/Mrad, was obtained by subtracting the rate of oxygen accumulation at zero time after irradiation, cc$(O_2)_z$/Mrad (bottommost curve in Figure 6), from the total rate of oxygen accumulation as given by the upper-most curve, cc(O_2) th. eq./Mrad, as follows:

$$0.30 \times 10^{-2} \text{cc } (O_2) \text{ th. eq./g-Mrad} - 0.065 \times 10^{-2} \text{cc } (O_2)_z\text{/g-Mrad} =$$

$$0.235 \times 10^{-2} \text{cc}(O_2)_n\text{/g-Mrad}$$

or 0.235×10^{-2} cc $(O_2)_n$/g-Mrad x 0.41 Mrad/hour =

$$0.096 \times 10^{-2} \text{ cc } (O_2)_n\text{/g-hr}$$

Here again, the net rate of N_2O_5 formation must be corrected by adding to it the rate of formation represented by the net rate of N_2O_5 decomposition after irradiation. The net rate of N_2O_5 decomposition was obtained by multiplying the rate constant of N_2O_5 decomposition, 1.0×10^{-5} sec^{-1} by the difference in the decomposition rate concentrations of O_2 at 49 Mrads, given by

$$\left[\frac{(O_2)_{\text{th. eq.}}}{g} - \frac{(O_2)_z}{g}\right] \quad \text{, viz.,}$$

$$1.0 \times 10^{-5} \frac{1}{\text{sec}} \times 3.6 \times 10^{3} \frac{\text{sec}}{\text{hr}} \times \frac{(0.134 \text{ cc } (O_2)_{\text{th. eq.}}}{g} - \frac{0.014\text{cc}(O_2)_z}{g} =$$

$$3.6 \times 10^{-2} \frac{1}{\text{sec}} \times 0.12\text{cc} \frac{(O_2)_n}{g} = 0.432 \times 10^{-2} \text{ cc } \frac{(O_2)_n}{\text{g-hr}}$$

The total rate of N_2O_5 formation is, therefore,

$$0.096 \times 10^{-2} \frac{\text{cc }(O_2)_n}{\text{g-hr}} + 0.432 \times 10^{-2} \frac{\text{cc }(O_2)_n}{\text{g-hr}} = 0.528 \frac{\text{cc }(O_2)_t}{\text{g-hr}}$$

Dividing by the dose rate, the total rate of N_2O_5 formation is given in terms of cc (O_2) / g-Mrad, i.e.,

$$0.528 \text{ cc } (O_2)/\text{g-hr} \times \text{hr}/0.41 \text{ Mrad} = 1.29 \times 10^{-2} \text{ cc } (O_2)/\text{g-Mrad}$$

and finally,

$$G(N_2O_5) = \frac{2 \times 1.29 \times 10^{-2} \times 6.02 \times 10^{23}}{2.24 \times 10^{4} \times 6.24 \times 10^{17}} = 1.11.$$

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