

# **Radiation Chemistry of Nitrous Oxide Gas**

## **Primary Processes, Elementary Reactions, and Yields**

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## Foreword

The National Standard Reference Data System provides access to the quantitative data of physical science, critically evaluated and compiled for convenience and readily accessible through a variety of distribution channels. The System was established in 1963 by action of the President's Office of Science and Technology and the Federal Council for Science and Technology, and responsibility to administer it was assigned to the National Bureau of Standards.

NSRDS receives advice and planning assistance from a Review Committee of the National Research Council of the National Academy of Sciences-National Academy of Engineering. A number of Advisory Panels, each concerned with a single technical area, meet regularly to examine major portions of the program, assign relative priorities, and identify specific key problems in need of further attention. For selected specific topics, the Advisory Panels sponsor subpanels which make detailed studies of users' needs, the present state of knowledge, and existing data resources as a basis for recommending one or more data compilation activities. This assembly of advisory services contributes greatly to the guidance of NSRDS activities.

The System now includes a complex of data centers and other activities in academic institutions and other laboratories. Components of the NSRDS produce compilations of critically evaluated data, reviews of the state of quantitative knowledge in specialized areas, and computations of useful functions derived from standard reference data. The centers and projects also establish criteria for evaluation and compilation of data and recommend improvements in experimental techniques. They are normally associated with research in the relevant field.

The technical scope of NSRDS is indicated by the categories of projects active or being planned: *nuclear properties, atomic and molecular properties, solid state properties, thermodynamic and transport properties, chemical kinetics, and colloid and surface properties.*

Reliable data on the properties of matter and materials is a major foundation of scientific and technical progress. Such important activities as basic scientific research, industrial quality control, development of new materials for building and other technologies, measuring and correcting environmental pollution depend on quality reference data. In NSRDS, the Bureau's responsibility to support American science, industry, and commerce is vitally fulfilled.

*RICHARD W. ROBERTS, Director*

## Preface

This report is one of a series of data publications on radiation chemistry; the aim of the series is to compile, evaluate, and present the numerical results on processes occurring in systems which have been subjected to ionizing radiation. Various kinds of data are important in radiation chemistry. The quantities which were measured first were the observed radiation yields or  $G$  values (molecules formed or destroyed per 100 eV). Various indirect methods based on  $G$  values have been used to determine yields of transient species and relative rates of reactions. The spectral properties (optical, electron spin resonance) of transients have provided a direct method for their identification, and rates of the very fast reactions of transients which occur in irradiated systems have been measured directly by spectroscopic methods. Conductivity and luminescence methods have also provided a means of measuring properties of transients and their kinetics. Some reactions which occur in irradiated systems have also been studied by other methods, such as photochemistry, electric discharge, ultrasonics, chemical initiation, electron impact, etc. The emphasis in these publications is on the data of radiation chemistry, but where other pertinent data exist, they are included.

The data of radiation chemistry are voluminous; thousands of systems have been investigated. As a result there are certain collections, *e.g.* rate constants of particular types of reactions or certain properties of transients, for which tabulations of the data are considered essential, but for which critical assessment of each value is impossible. On the other hand, certain systems and properties have been studied so extensively that critical examination of these data is desirable and timely. Authors of this series of data publications have been asked to evaluate the extent to which the data can be critically assessed, to describe their criteria for evaluation, and to designate preferred values whenever possible.

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# **Radiation Chemistry of Nitrous Oxide Gas**

## **Primary Processes, Elementary Reactions and Yields\***

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Data on the radiation yields from nitrous oxide gas, and the effects of variables, including dose-rate, total dose, pressure, temperature, applied fields and scavengers are reviewed. The use of  $N_2O$  as a gas-phase, chemical dosimeter is discussed. Primary processes in irradiated  $N_2O$  are discussed and elementary reactions, relevant to the system, are listed.

Key words: Chemical kinetics; data compilation; dosimetry; G; gas; nitrous oxide; radiation chemistry; rates; review.

### **1. Introduction**

Although radiolysis of nitrous oxide was first studied over half a century ago (19-0001) a complete mechanism cannot yet be written. To a large extent, this is a consequence of the complexity of the system and, at the present time, collection of the available data on nitrous oxide cannot be justified either on the grounds of completeness or by the hope that the collection may precipitate a full interpretation. Nevertheless, in spite of the many deficiencies and discrepancies in present knowledge of the nitrous oxide system, the information available is of significance because of the two important roles of nitrous oxide in radiation chemistry: as a gas-phase chemical dosimeter and as a selective electron scavenger in a variety of systems. It is for this reason that this data survey has been prepared.

The aim is to present the available data on the radiation yields from nitrous oxide and on the effects of important variables on the yields. The reactions which may occur in the system are listed, with the information about their rate constants that is available from independent sources. No attempt is made here to interpret the yields in terms of a reaction mechanism.

The reference numbers are the reference code numbers assigned by the Radiation Chemistry Data Center.

### **2. Primary Processes**

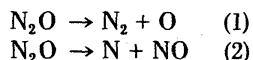
#### **2.1. Electronic Excitation**

Much of the information about the chemical consequences of electronic excitation of  $N_2O$  is obtained from spectroscopic and photochemical studies. The optical absorption spectrum is highly structured in the region (123.6 to 184.9 nm) normally used for photochemical studies (53-9004), suggesting that the excited states are not all dissociative. However, there is no evidence that excited  $N_2O$  molecules participate in the photochemistry prior to their dissociation.

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\*This is a data review prepared for, and in cooperation with, the Radiation Chemistry Data Center of the Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556. The Laboratory is operated under contract with the Atomic Energy Commission. The work of the Center is supported in part by the National Bureau of Standards, Office of Standard Reference Data.

The electron impact excitation spectrum of  $N_2O$  shows transitions corresponding to levels observed in the optical spectrum; a forbidden transition, probably to a triplet state, was observed at 4.4 eV (71-9364). The known photochemistry of  $N_2O$  can be interpreted with reasonable success in terms of the primary reactions (1) and (2):



The products of these reactions can be in a variety of excited states. The threshold energies for production of the different excited states are given in table 2.1.

Recent experimental work using high dose rate electron pulses has given information about the extent of the contribution of excitation processes to the net radiolytic decomposition (72-0088). The conclusions are summarized in table 2.2.

TABLE 2.1. Threshold energies (eV) for  $N_2O$  decomposition (64-7008)

$N_2 (N_2O \rightarrow N_2 + O)$				
O	$X^1\Sigma$	$A^3\Sigma_u^+$	$B^3\Pi_g$	$a^1\Pi_g$
$^3P$	1.67 <sup>a</sup>	7.89	9.03	10.23
$^1D$	3.64	9.86	11.00	12.20
$^1S$	5.86	12.08 <sup>a</sup>	13.22 <sup>a</sup>	14.11
$NO (N_2O \rightarrow NO + N)$				
N	$X^2\Pi$	$A^2\Sigma^+$	$B^2\Pi$	
$^4S$	5.02 <sup>a</sup>	5.42 <sup>a</sup>	5.61 <sup>a</sup>	
$^2D$	7.40	7.80	7.99	
$^2P$	8.60	9.00	9.19	

a. Optical transition is spin forbidden.

$D(NN-O) = 1.67$  eV (67-9124)

$D(N-NO) = 4.99$  eV (62-9017)

## 2.2. Ionization

Table 2.3 gives the yields of positive ions in  $N_2O$ , calculated from  $W(N_2O) = 32.9 \pm 0.4$  eV per ion pair (64-0177) and the ion fragmentation pattern, determined in a low pressure mass spectrometer at 70 eV (65-0483). This may not be a true representation of the radiolytic ion yields, since the extent of fragmentation may be less at the higher pressures used in the radiolysis. No information appears to be available from mass spectrometry at higher pressures.

TABLE 2.2 Dissociation of neutral excited molecules in irradiated  $N_2O$  (Pulsed irradiation at high dose rate ( $10^{26} - 10^{28}$  eV  $g^{-1}s^{-1}$ ) 72-0088)

Reaction	$C(\text{reaction})/\text{molecules } (100 \text{ eV})^{-1}$
$N_2O \rightarrow N_2(X^1\Sigma) + O(^1D)$ (or $^1S$ )	4.00
$N_2O \rightarrow N_2(A^3\Sigma) + O(^3P)$	0.81
$N_2O \rightarrow N(^2D) + NO$	0.05

NOTE: These values were not measured directly but are derived from product yield measurements making several assumptions about the reaction mechanism. For a detailed discussion see reference 72-0088.



### 2.3. Electron Capture

The rate of electron capture by  $N_2O$ , the nature of this process and its chemical consequences are still the subjects of active experimentation and discussion and clearly it will be some time before the last word is said on these matters. Discussions of recent work can be found in references 72-0449 and 72-9150.

It is generally agreed that, at least in the pressure region above about 20 torr, capture of thermal electrons occurs predominantly by a pseudo three body process (3) (68-9042, 68-9078).



The apparent rate constant  $k_3 = (2.01 \pm 0.07) \times 10^9 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-2}$  (68-9042).

Attachment by a two-body dissociative process, reaction (3a)



also occurs in  $N_2O$ . Recent rate measurements (72-0449) give  $k_{3a} = 3.6 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  (298 K). Reaction (3a) is 0.21 eV endothermic and it has been suggested that the zero energy capture process might be due to attachment to the few  $N_2O$  molecules with internal vibrational energy above the threshold value (67-9124, 69-9031, 69-9136). The temperature dependence of precise data in the range 278-355 K fits the relationship  $k_{3a} = 4.4 \times 10^{13} \exp(-4.8 \times 10^3/T) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  giving an activation energy for attachment of  $0.42 \pm 0.04 \text{ eV}$ . These data, taken together with data at high temperatures fit the relationship  $k_{3a} = 1.5 \times 10^{13} \exp(-4.6 \times 10^3/T) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  over the range 278-2900 K (72-0449).

The products from reactions (3) and (3a) are discussed in section 3.3.

TABLE 2.3. Yields of primary ions from  $N_2O$

Ion	Accompanying Neutral Species	$G/\text{molecules}(100\text{eV})^{-1}$	
		a	b
$N_2O^+$	-	1.98	1.90
$NO^+$	N	0.61	0.59
$N^+$	NO	0.21	0.25
$O^+$	$N_2$	0.09	0.10
$N_2^+$	O	0.15	0.21
$e^-$	-	3.04	3.04

NOTE: Values based on ion pair yield calculated from the energy required per ion pair  $W(N_2O) = 32.9 \pm 0.4 \text{ eV}$  (64-0177) using mass spectral data from a (65-0483), b (66-9163).

## 3. Elementary Reactions

The elementary reactions participating in  $N_2O$  radiolysis can, at present, be deduced only by making assumptions about the nature of the primary processes and of the reactive intermediates given by such processes. The available information about the various possible intermediates is summarized in tables 3.1, 3.2, and 3.3. The extent to which any of these reactions is involved in  $N_2O$  radiolysis is not known and, of course, will depend to some extent on the reaction conditions.

### 3.1. Neutral Species

See table 3.1.

### 3.2. Positive Ions

See table 3.2.

TABLE 3.1. Elementary reactions. Neutral species at room temperature

Species	Reaction	Rate Constant/ dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> (second order) dm <sup>6</sup> mol <sup>-2</sup> s <sup>-2</sup> (third order) s <sup>-1</sup> (first order)	Reference	Note
O( <sup>3</sup> P)	O + N <sub>2</sub> O → N <sub>2</sub> + O <sub>2</sub>	—	69-9080	a
	O + N <sub>2</sub> O → 2 NO	—	69-9080	a
	O + NO + M → NO <sub>2</sub> + M	3.7 × 10 <sup>10</sup>	64-9021	
	O + NO <sub>2</sub> → NO + O <sub>2</sub>	2.1 × 10 <sup>9</sup>	57-7006	
	O + O <sub>2</sub> + M → O <sub>3</sub> + M (M = N <sub>2</sub> O)	5.4 × 10 <sup>8</sup>	68-9063	
	O + O + M → O <sub>2</sub> + M	2.6 × 10 <sup>9</sup>	68-9063	d
	O + N( <sup>4</sup> S) + M → NO + M	4 × 10 <sup>9</sup>	67-9126	d
O( <sup>1</sup> D)	O* + N <sub>2</sub> O → N <sub>2</sub> + O <sub>2</sub>	4.2 × 10 <sup>10</sup>	68-7198	b
			70-7558	
O( <sup>1</sup> S)	O* + N <sub>2</sub> O → 2NO	7.8 × 10 <sup>10</sup>	68-7198	b
	O* + NO → O( <sup>3</sup> P) + NO	9 × 10 <sup>10</sup>	68-7198	
	O* + O <sub>2</sub> → O( <sup>3</sup> P) + O <sub>2</sub>	2.4 × 10 <sup>10</sup>	68-7198	
N( <sup>4</sup> S)	O* + N <sub>2</sub> O → O( <sup>3</sup> P) + N <sub>2</sub> O	9.6 × 10 <sup>9</sup>	68-7198	
	O* + NO → O( <sup>3</sup> P) + NO	3.3 × 10 <sup>11</sup>	68-7198	
N( <sup>2</sup> D)	N + N <sub>2</sub> O → N <sub>2</sub> + NO	< 10 <sup>5</sup>	57-9008	
	N + NO → N <sub>2</sub> + O	1.8 × 10 <sup>10</sup>	69-9080	c
	N + N + M → N <sub>2</sub> + M (M=N <sub>2</sub> )	3 × 10 <sup>9</sup>	67-9126	d
	N + O + M → NO + M (M=N <sub>2</sub> )	4 × 10 <sup>9</sup>	67-9126	d
N <sub>2</sub> ( <sup>3</sup> Σ <sub>g</sub> <sup>+</sup> )	N* + N <sub>2</sub> O → N <sub>2</sub> + NO	1.8 × 10 <sup>9</sup>	69-6025	
	N* + NO → N <sub>2</sub> + O( <sup>3</sup> P)	1.1 × 10 <sup>11</sup>	69-6025	
	N* + NO → N( <sup>4</sup> S) + NO	< 3.6 × 10 <sup>6</sup>	69-6025	
N <sub>2</sub> ( <sup>3</sup> Π <sub>g</sub> )	N <sub>2</sub> * → N <sub>2</sub> + hν	8.3 × 10 <sup>-2</sup>	67-9127	
	N <sub>2</sub> * + N <sub>2</sub> O → N <sub>2</sub> + N <sub>2</sub> O	3.8 × 10 <sup>9</sup>	69-7003	e
	N <sub>2</sub> * + NO → N <sub>2</sub> + NO(A <sup>2</sup> Σ)	4.2 × 10 <sup>10</sup>	69-7003	
	N <sub>2</sub> * + N <sub>2</sub> O → 2N <sub>2</sub> ( <sup>1</sup> Σ) + O( <sup>1</sup> S)	9.6 × 10 <sup>10</sup>	69-7003	
	N <sub>2</sub> * + NO → N <sub>2</sub> + NO	1.4 × 10 <sup>11</sup>	69-7003	

a. Negligible at temperatures used in radiolysis.

b. Rate constants calculated from the absolute rate constant for deactivation of O(<sup>1</sup>D) by H<sub>2</sub>O (68-7198) and relative constants for the two reactions of O(<sup>1</sup>D) with N<sub>2</sub>O (70-7558); cf. also 71-7213.

c. Recommended rate constant  $k = 3.1 \times 10^{10} \exp(-334/RT) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  (R in cal mol<sup>-1</sup>K<sup>-1</sup>). (69-9080).

d. No values reported for M = N<sub>2</sub>O.

e. From quantum yield in N<sub>2</sub>O photolysis at 147 nm (71-7181) it is concluded that deactivation of N<sub>2</sub>(<sup>3</sup>Σ) by N<sub>2</sub>O results in dissociation of N<sub>2</sub>O (→ N<sub>2</sub> + O). See 71-7181 for discussion of previous evidence for this reaction.

### 3.3. Negative Ions

At very high dose rates electron capture by N<sub>2</sub>O does not compete effectively with ion-electron neutralization and negative ion reactions do not occur (72-0088).

At low dose rates, where electron capture can occur, the negative ion reactions may be of considerable significance (65-0483, 70-0384, 72-0088, 72-0449, 72-9150). However, the negative ion reactions in N<sub>2</sub>O are rather complicated and not well understood. For detailed accounts of the information available references 72-0449 and 72-9150 should be consulted.

It has been suggested (68-9042) that N<sub>2</sub>O<sup>-</sup> might be formed by the three-body electron capture reaction (3). This ion has not been directly observed as a product of electron capture, although it has been observed in a mass spectrometer under conditions where it is formed as a result of the reaction of O<sup>-</sup> with N<sub>2</sub>O (66-9042). At low pressures (up to 20 torr) the third order

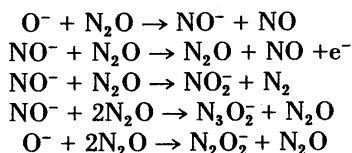
TABLE 3.2. Elementary reactions. Positive ions

Species	Reaction	Rate Constant /dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	Reference	Note
N <sub>2</sub> O <sup>+</sup>	N <sub>2</sub> O <sup>+</sup> + N <sub>2</sub> O → 2N <sub>2</sub> + O <sub>2</sub> <sup>+</sup>	—	—	a
	N <sub>2</sub> O <sup>+</sup> + N <sub>2</sub> O → N <sub>2</sub> + NO <sup>+</sup> + NO	—	67-9129	b
	N <sub>2</sub> O <sup>+</sup> + NO → N <sub>2</sub> O + NO <sup>+</sup>	—	—	a
	N <sub>2</sub> O <sup>+</sup> + O <sub>2</sub> → N <sub>2</sub> O + O <sub>2</sub> <sup>+</sup>	—	—	a
N <sub>2</sub> <sup>+</sup>	N <sub>2</sub> <sup>+</sup> + N <sub>2</sub> O → N <sub>2</sub> + N <sub>2</sub> O <sup>+</sup>	3.0 x 10 <sup>11</sup>	70-9074	
	N <sub>2</sub> <sup>+</sup> + N <sub>2</sub> O → NO <sup>+</sup> + N <sub>2</sub> + N	2.4 x 10 <sup>11</sup>	70-9074	
	N <sub>2</sub> <sup>+</sup> + O <sub>2</sub> → N <sub>2</sub> + O <sub>2</sub> <sup>+</sup>	2.8 x 10 <sup>10</sup>	70-9074	
	N <sub>2</sub> <sup>+</sup> + NO → N <sub>2</sub> + NO <sup>+</sup>	3.0 x 10 <sup>11</sup>	70-9074	
O <sup>+</sup>	O <sup>+</sup> + N <sub>2</sub> O → N <sub>2</sub> O <sup>+</sup> + O	2.4 x 10 <sup>11</sup>	70-9074	
	O <sup>+</sup> + N <sub>2</sub> O → O <sub>2</sub> <sup>+</sup> + N <sub>2</sub>	1.2 x 10 <sup>10</sup>	70-9074	
	O <sup>+</sup> + N <sub>2</sub> → NO <sup>+</sup> + N	7.8 x 10 <sup>7</sup>	70-9074	
	O <sup>+</sup> + NO → NO <sup>+</sup> + O	≤ 1.5 x 10 <sup>10</sup>	70-9074	
	O <sup>+</sup> + O <sub>2</sub> → O <sub>2</sub> <sup>+</sup> + O	1.2 x 10 <sup>10</sup>	70-9074	
N <sup>+</sup>	N <sup>+</sup> + N <sub>2</sub> O → NO <sup>+</sup> + N <sub>2</sub>	3.0 x 10 <sup>11</sup>	70-9074	
	N <sup>+</sup> + O <sub>2</sub> <sup>+</sup> + N	3.0 x 10 <sup>11</sup>	70-9074	
	N <sup>+</sup> + O <sub>2</sub> → NO <sup>+</sup> + O	3.0 x 10 <sup>11</sup>	70-9074	
	N <sup>+</sup> + NO → NO <sup>+</sup> + N	4.8 x 10 <sup>11</sup>	70-9074	

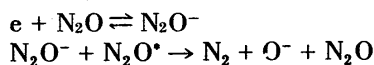
a. Reactions feasible on energetic grounds but no rate data reported.

b. Reaction cross-section 6.3 x 10<sup>-17</sup> cm<sup>2</sup>.

attachment process may be a consequence of the second order attachment reaction (3a) and a sequence involving the following negative ion reactions (72-9150):

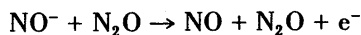


At high pressures (above 20 torr) it is necessary to postulate the formation, as a product of reaction (3), of an ion which can detach an electron:



(where N<sub>2</sub>O\* is a molecule with sufficient energy to make the forward reaction endoergic) (72-9150).

The significance of the electron detachment reaction:



has been demonstrated (72-0449) and the possible contribution of the reaction:



(followed by electron detachment from NO<sup>-</sup>) to the chain decomposition of N<sub>2</sub>O at low temperatures and high pressures has been discussed (72-0449). (See also sections 5.2 and 5.3.) Elementary reactions of negative ions are collected in table 3.3.

### 3.4. Neutralization Reactions

Ion lifetime measurements in N<sub>2</sub>O indicate that ion clustering can complicate the recombination process (70-0046, 72-9150) and this is of importance at low dose rates. Attempts

have been made to deduce information about the chemical consequences of ion neutralization at low dose rates by studying the effects of electron scavenging additives (70-0413). This approach has not been successful, mainly because of a lack of knowledge of the effects of such additives on reactions other than ion neutralization and also because the reactions of the negative species from  $N_2O$  are not understood.

Complications due to secondary reactions of the ions can largely be avoided by using very high dose rates (72-0088). The main reactions occurring under these conditions are summarized in table 3.4.

TABLE 3.3. Elementary reactions. Negative ions

Species	Reaction	Rate Constant $/dm^3 mol^{-1} s^{-1}$	Reference	Note
$N_2O^-$ $O^-$	$N_2O^- + O_2 \rightarrow O_3^- + N_2$	fast	69 9135	
	$O^- + N_2O \rightarrow N_2 + O_2^-$	—	64-9020	a
	$O^- + N_2O \rightarrow NO^- + NO$	$1.2 \times 10^{11}$	68-9071	
	$O^- + N_2O \rightarrow NO_2^- + N$	$2.4 \times 10^8$	66-9042	b
	$O^- + N_2O \rightarrow N_2O^- + O$	$1.2 \times 10^{10}$	66 9042	
	$O^- + NO_2 \rightarrow NO_2^- + O$	$6 \times 10^{11}$	66-9042	
	$O^- + 2N_2O \rightarrow N_2O_2^- + N_2O$	$1.5 \times 10^{19} (dm^6 mol^{-2} s^{-2})$	72-9150	
	$O^- + N_2O \rightleftharpoons (N_2O_2^-)^*$	$2.4 \times 10^9$	68-9071	c
	$(N_2O_2^-) \rightarrow NO^- + NO$	$2.5 \times 10^6$	68-9071	c
	$NO^-$	$NO^- + 2N_2O \rightarrow N_3O_2^- + N_2O$	$3.1 \times 10^{18} (dm^6 mol^{-2} s^{-2})$	72-9150
$NO^- + N_2O \rightleftharpoons (N_3O_2^-)^* \rightarrow N_3O_2^-$		$3 \times 10^8$	68-9071	c
$NO^- + N_2O \rightarrow NO_2^- + N_2$		$6 \times 10^9$	68-9071	
$NO^- + N_2O \rightarrow N_2O + NO + e^-$		$3.6 \times 10^9$	72-9150	c

a. The occurrence of this reaction is doubtful for ions of thermal energies (66-9042, 70-9229).

b. The reported formation of  $NO_2^-$  may be due to  $O^- + NO_2 \rightarrow NO_2^- + O$  (66-9042).

c. Reaction assumed in the interpretation of the formation of ions observed in drift tubes.

TABLE 3.4. Ion neutralization reactions in irradiated  $N_2O$  (Pulsed irradiation at high dose rate ( $10^{26} - 10^{28} eV g^{-1} s^{-1}$ ) 72-0088)

Reaction	$G(\text{reaction})/\text{molecules } (100 eV)^{-1}$
$NO^+ + e^- \rightarrow N(^2D) + O(^3P)$	0.73
$NO^+ + e^- \rightarrow N(^4S) + O(^1D)$	0.20
$N_2O^+ + e^- \rightarrow N_2(^1\Sigma) + O(^1D)$	1.20
$N_2O^+ + e^- \rightarrow N_2(^3\Pi) + O(^3P)$	0.55
$N_2O^+ + e^- \rightarrow N(^2D) + NO$	0
$N_2O^+ + e^- \rightarrow N_2(^3\Sigma) + O(^3P)$	0.37

NOTE: These values were not measured directly but are derived from observed product yield on the basis of several assumptions about the reaction mechanism. For a detailed discussion see reference 72-0088.

## 4. Product Yields Under Dosimeter Conditions

### 4.1. Nitrogen

$N_2O$  has been recommended as a gas-phase chemical dosimeter (56-0023). For this purpose,  $N_2O$  is irradiated at pressures in the region of 760 torr and room temperature (290 - 300 K). Determination of  $N_2$  rather than any of the other products is recommended for dosimeter purposes because the analysis of  $N_2$  presents no practical difficulties. Preferably, the total dose should not exceed  $10^{20} eV g^{-1}$  ( $N_2O$  conversion ca. 0.1 mol percent).

Reported absolute values of  $G(N_2)$  for dose rates up to  $10^{18}$  eV  $g^{-1}s^{-1}$  are given in table 4.1. (For very high dose rate, pulsed irradiation see table 4.4).

Of the various methods of measurement of energy absorption, ionization-current measurement is the most direct and capable of greatest accuracy (66-0434). The preferred value (table 4.1) is based on the most reliable determination using this method. For details of ionization chamber design see 56-0024. For a discussion of the calculation of gas-phase dose from solution dosimetry see 62-0146 and 63-0195.

TABLE 4.1. Initial  $G(N_2)$  (Dose rates up to  $10^{18}$  eV  $g^{-1}s^{-1}$ )

$G(N_2)$	Source	$10^{15}$ Dose Rate /eV $g^{-1}s^{-1}$	$10^{20}$ Max. Dose <sup>i</sup> /eV $g^{-1}$	Max. Conv. <sup>i</sup> /mol percent $N_2O$	$P(N_2O)$ /torr	T/K	Dosime- try	Anal.	Ref.
$11.5 \pm 0.4^a$	$\gamma$	2.7	1.4	0.14	760	room	F	C,M	62-0146
$12.8 \pm 0.4^b$	$\gamma$	2.7	3.3	0.33	760	room	I	C,M	62-0146
$10.7 \pm 0.7^c$	$\gamma$	10	2.7	0.3	760	287-295	F	G	61-0103
$9.9 \pm 0.8^d$	$\gamma$	30	-	-	250-1000	298	-	C	63-0195
$9.9 \pm 0.5$	$\gamma$	2.1	0.27	0.02	660-1000	283	F	C,G	69-0085
10.1	$\gamma$	8.3	7.2	-	50-400	298	F	C,G	70-0413
$9.8^e$	$\gamma$	150	1.1	0.1	149	303	I	C,M	65-0483
$10.15^f$	X (70 kV)	0.01	-	-	200,555	room	I	C	58-0056
$10.9 \pm 1.0$	X (4 MeV)	150	2.7	0.3	20-664	room	C	G	61-0103
$10.0 \pm 0.2^g$	$e^-$ (1 MeV)	$10^2 - 10^3$	1.0	0.1	200,600	297	I	C,A	66-0434
$11.3 \pm 0.5$	$\beta^-$ (T)	0.1 - 7	2.7	0.3	760	room	S	C	61-0103
$10.0 \pm 0.4$	$\alpha$ ( $^{210}Po$ )	2	0.43	0.04	440-680	298	S	C,G	69-0085
$10.6 \pm 0.5^h$	$\alpha$ (Rn)	0.2	2.4	0.2	100,200	303	I	C	48-0003

Preferred value  $G(N_2) = 10.0 \pm 0.2$

Conditions:  $N_2O$  pressure = 100 - 1000 torr

Temperature = 290 - 300 K

$N_2O$  conversion  $\leq$  0.1 mol percent

Total dose  $\leq$   $1 \times 10^{20}$  eV  $g^{-1}$

Dosimetry: F = Fricke dosimeter, C = Ceric sulphate dosimeter, I = Ionization current determination, S = Radioisotope calibration

Analysis: C = Trapping of condensables at 77 K, M = Mass spectrometry, G = Gas chromatography, A = Combustion analysis.

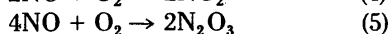
- $G(N_2)$  from table 1 in paper.
- High  $G(N_2)$  is attributable to incomplete ion collection in the ionization chamber used (see 66-0434). Redesigned ionization chamber gave  $G(N_2) = 10.0 \pm 0.2$  (G.R.A. Johnson and M. Simic, unpublished results).
- Values from table 1 in paper. Abnormally high  $G(N_2)$  was observed in glass vessels with wall-to-wall distance less than about 1 cm. An opposite effect, i.e., low  $G(N_2)$  in vessels packed with glass tubes, has been reported (66-0312).
- Method of energy measurement not stated. Residual gas yield measured after trapping at 77 K but not analyzed.  $G(N_2)$  given here is calculated assuming  $G(O_2, \text{ after trapping}) = 2.0 \pm 0.1$  (see sec. 4.2).
- Recalculated using  $W(N_2O) = 32.9$ .
- $G(N_2)$  calculated from  $M/N = 4.0$  reported for residual gas yield after trapping at 77 K, assuming  $W(N_2O) = 32.9$  eV and  $G(O_2, \text{ after trapping}) = 2.0 \pm 0.1$ . Author's calculations, based on results with added NO or  $O_2$ , gave  $G(N_2) = 11.3$ .
- Preferred value. Dose calculated using  $W(N_2O) = 32.9 \pm 0.4$  eV (ion pair) $^{-1}$  (64-0177).
- $G(N_2)$  calculated from  $M/N = 4.0 \pm 0.2$  given for the total yield of gases after trapping at 77 K, assuming  $W(N_2O) = 32.9$  and  $G(O_2, \text{ residual}) = 2.0$ .
- Maximum dose and conversion at which the quoted  $G(N_2)$  is stated to be valid.

## 4.2. Oxygen

The products from  $N_2O$  radiolysis, other than  $N_2$ , are  $O_2$ , NO, and  $NO_2$ . The possibility of chemical reaction between  $O_2$  and NO makes it difficult to decide whether  $NO_2$  is a primary product or is formed by secondary reactions between  $O_2$  and NO. This uncertainty complicates the analysis of these products.

For O<sub>2</sub> determination, gas analysis, after trapping the condensable gases at 77 K, has usually been employed (62-0146, 69-0085, 70-0413, 66-0434) but direct gas chromatography without trapping has also been used (61-0103).

NO reacts with O<sub>2</sub> relatively slowly at room temperature. On cooling to 77 K reactions (4) and (5) occur, probably enhanced by mercury which is often present (58-0056).



Thawing, followed by refreezing, causes decomposition of N<sub>2</sub>O<sub>3</sub> by reaction (6).



so that the final stoichiometry of the reaction corresponds to reaction (4). The reaction of NO with O<sub>2</sub> under the conditions used for gas chromatographic analysis is uncertain. It has been suggested (61-0103) that the extent of reaction is negligible. However, evidence for quantitative occurrence of a process of overall stoichiometry corresponding to reaction (5) has been obtained (71-7181).

#### 4.2.1. Oxygen and Nitric Oxide Yields

In most determinations, the residual O<sub>2</sub> yield, i.e., the O<sub>2</sub> remaining, after trapping condensable gases at 77 K, has been measured. There is reasonable agreement between determinations of this quantity. The recommended value  $G(\text{O}_2, \text{measured}) = 2.0 \pm 0.2$ , selected for the reasons given for the preferred  $G(\text{N}_2)$ .

Table 4.2 gives reported values of the O<sub>2</sub> yields. Values of  $G(\text{O}_2)$  have been calculated from  $G(\text{O}_2, \text{measured})$ . Where  $G(\text{O}_2, \text{measured})$  is from the residual gas yield after condensing at 77 K,  $G(\text{O}_2)$  was calculated assuming that the stoichiometry of the trap reaction is represented by reaction (4) and that NO<sub>2</sub> and other nitrogen oxides are not formed directly as radiation products.

TABLE 4.2. Initial O<sub>2</sub> yields (Dose rates up to 10<sup>18</sup>eVg<sup>-1</sup>s<sup>-1</sup>)

$G(\text{O}_2, \text{meas.})$	$G(\text{O}_2)$	Source	10 <sup>-15</sup> Dose Rate /eV g <sup>-1</sup> s <sup>-1</sup>	10 <sup>-20</sup> Max. Dose /eV g <sup>-1</sup>	P (N <sub>2</sub> O) /torr	T/K	Anal.	Ref.
1.9 ± 0.1 <sup>a,c</sup>	4.0 ± 0.2 <sup>a,c</sup>	γ	2.7	1.4	760	room	C,M	62-0146
2.6 ± 0.2 <sup>b,c</sup>	3.8 ± 0.3 <sup>b,c</sup>	γ	10	2.7	760	287-295	G	61-0103
1.8 ± 0.2 <sup>a,c</sup>	3.9 ± 0.4 <sup>a,c</sup>	γ	2.1	0.27	660-1000	283	C,G	69-0085
1.4 <sup>a</sup>	3.8 <sup>d</sup>	γ	8.3	7.2	200	298	C,G	70-0413
2.5 ± 0.3 <sup>b,c</sup>	3.8 ± 0.4 <sup>b,c</sup>	X (4 MeV)	150	2.7	20-664	room	G	61-0103
2.0 ± 0.2 <sup>a</sup>	4.0 ± 0.4 <sup>a</sup>	e <sup>-</sup> (1 MeV)	10 <sup>2</sup> - 10 <sup>3</sup>	1.2	600	297	C,A	66-0434
3.2 ± 0.2 <sup>b,c</sup>	4.1 ± 0.3 <sup>b,c</sup>	β <sup>-</sup> (T)	0.1 - 1.0	2.7	760	room	G	61-0103
2.0 ± 0.1 <sup>a</sup>	4.0 ± 0.2 <sup>a</sup>	α( <sup>210</sup> Po)	2	0.43	440-680	298	C,C	69-0085

Preferred values:  $G(\text{O}_2, \text{measured after trapping at 77 K}) = 2.0 \pm 0.2$   
 $G(\text{O}_2) = 4.0 \pm 0.4$

Conditions:

N<sub>2</sub>O pressure = 100 - 1000 torr

Temperature = 290 - 300 K

N<sub>2</sub>O conversion ≤ 0.1 mol percent

Total Dose < 1 × 10<sup>20</sup>eV g<sup>-1</sup>

Analysis: C = Trapping of condensables at 77 K, M = Mass spectrometry, G = Gas chromatography, A = Combustion analysis

- $G(\text{O}_2, \text{measured})$  is the residual O<sub>2</sub> yield after trapping at 77 K.  $G(\text{O}_2)$  is the calculated yield, assuming that the trap reaction is  $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ .
- $G(\text{O}_2, \text{measured})$  is the O<sub>2</sub> yield measured by direct gas chromatography of the irradiated gas.  $G(\text{O}_2)$  is the calculated yield, assuming the reaction during analysis is  $4\text{NO} + \text{O}_2 \rightarrow 2\text{N}_2\text{O}_3$ .
- Values corrected to  $G(\text{N}_2) = 10.0$ .
- $G(\text{O}_2)$  was calculated by authors; basis of calculation not fully explained but presumably similar to that in Note a.

Where  $G(\text{O}_2, \text{measured})$  is obtained by gas chromatography, it is assumed that reaction (5) occurs during analysis (71-7181).

### 4.3. Nitric Oxide

Values for the NO yield,  $G(\text{NO})$ , can be obtained from the residual  $\text{O}_2$  yield after trapping at 77 K,  $G(\text{O}_2, \text{measured})$ , assuming a stoichiometry for the trap reaction between NO and  $\text{O}_2$  (see sec. 4.2). Addition of a small amount of NO before irradiation has also been used to determine  $G(\text{NO})$ ; in this case the total gas yield after trapping is  $3/2 G(\text{NO}) + E(\text{NO})$  where  $E(\text{NO})$  is the amount of NO added, assuming the trap reaction corresponds to reaction (4) (58-0056).

$G(\text{NO})$  has also been determined (61-0103, 62-0146, 66-0434) by extracting a known quantity of the irradiated gas with aqueous sodium hydroxide solution in which the  $\text{NO}_3^-$  produced is measured by a spectrometric method. It is assumed that reaction (4) occurs rapidly in solution and that  $\text{NO}_3^-$  is formed according to reaction (7).

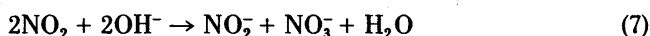


Table 4.3 summarizes values reported for NO yields. The preferred  $G(\text{NO}) = 4.0 \pm 0.4$  is selected on the basis of the preferred values for  $G(\text{N}_2)$  and  $G(\text{O}_2, \text{measured})$  together with the assumed stoichiometry of trap reactions. Directly measured values of  $G(\text{NO})$  are in fair agreement with this.

TABLE 4.3. Initial NO yield (dose rates up to  $10^{18} \text{eV g}^{-1} \text{s}^{-1}$ )

$G(\text{NO})$	Source	$10^{-15}$ Dose Rate $/\text{eV g}^{-1} \text{s}^{-1}$	$10^{-20}$ Max. Dose $/\text{eV g}^{-1}$	$\text{P}(\text{N}_2\text{O})$ $/\text{torr}$	T/K	Ref.
$3.7 \pm 0.3$ <sup>a,b</sup>	$\gamma$	2.7	1.4	760	room	62-0146
$4.5 \pm 0.7$ <sup>a,b,d</sup>	$\gamma$	10.0	2.7	760	288-295	61-0103
$4.2 \pm 0.5$ <sup>c,d</sup>	$\gamma$	2.1	0.27	660-1000	283	69-0085
$5.1$ <sup>b,c,e</sup>	$\gamma$	8.3	-	200	298	70-0413
$4.5 \pm 0.6$ <sup>b,c</sup>	X(4 MeV)	150	2.7	390-660	room	61-0103
$5.5 \pm 0.6$ <sup>a,b</sup>	$\beta$ (T)	0.1-1.0	2.7	760	room	61-0103
$4.0 \pm 0.2$ <sup>c</sup>	$\alpha$ ( $^{210}\text{Po}$ )	2.0	0.43	440-680	298	69-0085

Preferred value:  $G(\text{NO}) = 4.0 \pm 0.4$   
 Temperature = 290 - 300 K  
 $\text{N}_2\text{O}$  conversion  $\leq 0.1$  mol percent  
 Total dose  $\leq 1 \times 10^{20} \text{eV g}^{-1}$ .

- a. Analyzed as  $\text{NO}_3^-$  after dissolving in aqueous NaOH.
- b. Values corrected to  $G(\text{N}_2) = 10.0$ .
- c. Value from reported  $G(\text{O}_2, \text{measured})$  and  $G(\text{N}_2)$ .
- d. Apparent  $G$  depended on vessel volume; this value is for vessel with largest volume.
- e.  $G(\text{NO})$  calculated from their results by authors; basis of calculation not explained.

### 4.4. Yields at Very High Dose Rate

The very high dose rates obtained with electron pulses from field emission tubes ( $\geq 10^{27} \text{eV g}^{-1} \text{s}^{-1}$ ) give initial product yields which differ from those at lower dose rates. Calorimetric absolute dosimetry was used (68-0318, 71-0199) to obtain the values in table 4.4.

TABLE 4.4. Yields from very high dose rates (pulsed irradiation)

$G(N_2)$	$12.4 \pm 0.4$	$12.3 \pm 0.3$
$G(O_2, \text{measured})$	$2.5 \pm 0.3$	—
$G(O_2)$	$5.0 \pm 0.2^a$	—
$G(NO)$	$5.0 \pm 0.2^a$	—
$N_2O$ press/torr	380–760	~ 900 – 2000
Temp/K	298–325	296
Dose rate/eV $g^{-1}s^{-1}$	$10^{27}b$	$2 \times 10^{28}c$
Total dose/eV $g^{-1}$	$1.6 \times 10^{20}$	$5 \times 10^{19}$
Dosimetry	calorimetric	calorimetric
Reference	68–0318	71–0199

- Yield measured after trapping at 77 K;  $G(O_2)$  calculated assuming  $2NO + O_2 \rightarrow NO_2$  occurs as trap reaction.
- Delivered as electron pulse of half-height duration 30 ns (average electron energy 1 MeV, max. current 5000 A).
- Delivered as electron pulse of half-height duration of 3 ns, electron energy 600 keV, 200 A.

## 5. Effects of Conditions on Yields

### 5.1. Total Dose

Studies of the effect of total dose are few, but it is generally agreed that the  $G$ -values fall off as the total dose increases, presumably because of secondary radiolytic reactions involving the accumulating radiation products. At sufficiently low doses the  $G$  values of the products are independent of dose (within an uncertainty of about 10%), but the maximum dose to which this independence holds differs somewhat for different investigations, usually being between 1 and  $3 \times 10^{20}$  eV  $g^{-1}$  (tables 4.1–4.3).

Reported values for the dependence of yield on dose obtained in deliberate studies of total dose effects are summarized in table 5.1.

TABLE 5.1. Dependence of yields on total dose

$10^{-20}$ Dose /eV $g^{-1}$	$G(N_2)^a$	$G(O_2, \text{meas'd.})^b$	$P(N_2O)$ /torr	T/K	Dose rate /eV $g^{-1}s^{-1}$	Ref.
0.47	10.0	1.94	760	293	$2.7-5.0 \times 10^{15}$	62-0146
1.00	10.0	1.87	760	293	$2.7-5.0 \times 10^{15}$	62-0146
1.20	10.0	1.72	760	293	$2.7-5.0 \times 10^{15}$	62-0146
1.30	10.5	—	760	293	$2.7-5.0 \times 10^{15}$	62-0146
1.43	9.8	1.85	760	293	$2.7-5.0 \times 10^{15}$	62-0146
2.28	9.2	1.73	760	293	$2.7-5.0 \times 10^{15}$	62-0146
2.90	8.7	1.80	760	293	$2.7-5.0 \times 10^{15}$	62-0146
5.15	8.7	1.30	760	293	$2.7-5.0 \times 10^{15}$	62-0146
12.10	8.0	0.80	760	293	$2.7-5.0 \times 10^{15}$	62-0146
0.36	10.0	2.07	600	297	$1.25-10.0 \times 10^{17}$	66-0434
0.59	10.0	1.82	600	297	$1.25-10.0 \times 10^{17}$	66-0434
0.79	10.1	1.96	600	297	$1.25-10.0 \times 10^{17}$	66-0434
0.74	10.1	2.13	600	297	$1.25-10.0 \times 10^{17}$	66-0434
1.12	9.95	2.16	600	297	$1.25-10.0 \times 10^{17}$	66-0434
1.20	9.76	2.04	600	297	$1.25-10.0 \times 10^{17}$	66-0434
1.75	9.49	1.94	600	297	$1.25-10.0 \times 10^{17}$	66-0434
0.1	10.0	—	1500	300	$3 \times 10^{15}$	60-0119
1.0	8.7	—	1500	300	$3 \times 10^{15}$	60-0119
10.0	7.6	—	1500	300	$3 \times 10^{15}$	60-0119
100.0	6.65	—	1500	300	$3 \times 10^{15}$	60-0119
1000.0	5.7	—	1500	300	$3 \times 10^{15}$	60-0119

- Corrected assuming  $G(N_2) = 10.0$  at lowest total dose.
- Residual  $O_2$ , after trapping at 77 K.



## 5.2. Pressure

Relatively little work has been aimed specifically at determining the effect of  $N_2O$  pressure on the yields. A survey of the values given in tables 4.1–4.3 and summarized in table 5.2 suggests that the initial  $G(N_2)$ ,  $G(O_2)$ , and  $G(NO)$  are independent of  $N_2O$  pressure over the range 50 to 1000 torr  $N_2O$ , within an experimental uncertainty of about  $\pm 5\%$ .

TABLE 5.2. Effect of  $N_2O$  pressure on yields at room temperature

$P(N_2O)$ /torr	$G(N_2)$	$G(O_2, \text{measured})$	$G(O_2)$	$G(NO)$	Ref.
5	20.3	—	—	—	72-0449
10	16.2	0	5.0 <sup>d</sup>	12.2 <sup>d</sup>	70-0384
21	10.9	2.5	3.8	—	61-0103
24.5	14.0	—	—	—	72-0449
47.5	12.1	—	—	—	72-0449
50	9.5 <sup>a</sup>	0.86 <sup>a</sup>	3.45 <sup>d,e</sup>	5.2 <sup>d</sup>	66-0434
50	14.4	—	3.95	13.1	58-0056
50	10.1	—	—	—	70-0413
100	10.6	—	—	—	48-0003
149	9.8	—	—	—	65-0483
200	10.15	—	—	—	58-0056
200	10.0	1.64	3.9 <sup>d</sup>	4.5 <sup>d</sup>	66-0434
200	10.6	—	—	—	48-0003
250 <sup>b</sup>	9.9	—	—	—	63-0195
440 <sup>b</sup>	10.0	2.0	4.0 <sup>d</sup>	4.0 <sup>d</sup>	69-0085
555	10.15	—	—	—	58-0056
600	10.0	1.8	3.9 <sup>d</sup>	4.0 <sup>d</sup>	66-0434
600	9.9	—	—	—	69-0085
680 <sup>b</sup>	10.0	2.0	4.0 <sup>d</sup>	4.0 <sup>d</sup>	69-0085
760	11.5	1.9 <sup>e</sup>	4.0 <sup>d</sup>	3.7 <sup>e</sup>	62-0146
760	12.8	—	—	—	62-0146
760	10.7	2.6 <sup>e</sup>	3.8 <sup>f</sup>	4.5 <sup>e</sup>	61-0103
760	11.3	3.2 <sup>e</sup>	4.1 <sup>f</sup>	5.5 <sup>e</sup>	61-0103
1000 <sup>b</sup>	9.9	—	—	—	63-0195
1000 <sup>b</sup>	9.9	1.8	3.9	4.2	69-0085
$8.8 \times 10^3$	11.2 <sup>e</sup>	1.8	4.3	5.0	69-0085
$1.54 \times 10^4$	11.2 <sup>e</sup>	1.5	4.2	5.4	69-0085
$4.4 \times 10^4$	10.6 <sup>e</sup>	1.6	4.1	5.0	69-0085
$1.32 \times 10^5$	12.1 <sup>e</sup>	1.6	4.4	5.6	69-0085
$1.76 \times 10^5$	12.3 <sup>e</sup>	1.5	4.4	5.8	69-0085
$2.42 \times 10^5$	13.5 <sup>e</sup>	1.6	5.0	6.8	69-0085
$3.08 \times 10^5$	11.6 <sup>e</sup>	1.7	4.4	5.4	69-0085

a. Possibly not initial value.

b. Pressures quoted are upper and lower extremes of pressure-independent range.

c. Temperature = 311 K.

d. Calculated from residual yield after trapping at 77 K assuming trap reaction is  $2NO + O_2 \rightarrow 2NO_2$ .

e. Corrected to  $G(N_2) = 10.0$ .

f. Assuming  $4NO + O_2 \rightarrow 2N_2O_3$  on gas chromatography.

g. Measured as  $NO_3^-$  in solution.

Above 1000 torr  $N_2O$ , the only investigation carried out (69-0085) suggests that there is little, if any, change in the product yields up to  $3 \times 10^5$  torr  $N_2O$ .

Below 50 torr  $N_2O$ , there is evidence that  $G(-N_2O)$  increases and that the stoichiometry of the radiolytic decomposition differs from that at higher pressures (58-0056, 70-0384, 70-0239). Not all investigations found this effect of pressure (see 61-0103, 66-0434). It is possible that, in addition to pressure, some other variables may be involved in determining the mechanism in the low pressure region (e.g. temperature, surface or impurities). It has been shown (72-0449) that the

increased N<sub>2</sub>O decomposition at low pressures is eliminated by SF<sub>6</sub> (2%) suggesting that the electron is the primary species responsible. A chain reaction involving negative ions has been proposed (72-0449; see sec. 3.3).

High decomposition yields obtained when N<sub>2</sub>O was irradiated with 200 kV x-rays (60-0107) were subsequently shown to be attributable to an electrical discharge induced by electrical fields generated by the x-ray tube (62-0146).

### 5.3. Temperature

The effect of temperature on N<sub>2</sub>O radiolysis has not been systematically investigated at temperatures below 300 K. Reported yields indicate that there are no significant temperature effects in the normal ambient range (283 – 300 K).

Increased decomposition with increasing temperature above 300 K was reported in early work (19-0001) but relatively few studies of the effect of temperature have been carried out.

The extent of thermal (non-radiolytic) decomposition of N<sub>2</sub>O apparently depends upon the vessel surface. In stainless steel vessels, thermal decomposition becomes serious above 523 K (66-0434). In glass vessels, thermal decomposition is not significant below 673 K (65-0483).

The available data (summarized in table 5.3.1) suggest that (1) the radiolytic decomposition is increased by increasing temperature, (2) the stoichiometry changes, favouring an increase in the ratio  $G(\text{NO})/G(\text{O}_2)$  at elevated temperatures, (3) the effect of temperature is more marked at low N<sub>2</sub>O pressures, (4) the effect of temperature is less marked when very high dose-rate pulses are used.

TABLE 5.3.1. *Dependence of yields on temperature*

T/K	G(N <sub>2</sub> )	G(O <sub>2</sub> ) <sup>a</sup>	G(NO) <sup>a</sup>	P(N <sub>2</sub> O) /torr	10 <sup>-20</sup> Max. dose /eV g <sup>-1</sup>	Dose rate /eV g <sup>-1</sup> s <sup>-1</sup>	Ref.
297	10.0	4.0	4.0	400	1.1	1.5 x 10 <sup>17</sup>	66-0434
343	12.4	4.5	7.0	400	1.1	1.5 x 10 <sup>17</sup>	66-0434
373	14.1	4.9	8.8	400	1.1	1.5 x 10 <sup>17</sup>	66-0434
423	17.9	6.1	12.2	400	1.1	1.5 x 10 <sup>17</sup>	66-0434
473	21.1	7.2	14.2	400	1.1	1.5 x 10 <sup>17</sup>	66-0434
303	10.0 <sup>b</sup>	—	—	800	2.2	3 x 10 <sup>15</sup>	69-0534
373	14.0 <sup>b</sup>	—	—	800	2.2	3 x 10 <sup>15</sup>	69-0534
473	23.6 <sup>b</sup>	—	—	800	2.2	1.5 x 10 <sup>17</sup>	66-0434
313	10.0 <sup>b</sup>	3.2 <sup>a,c</sup>	7.0 <sup>c</sup>	50	1.1	3 x 10 <sup>15</sup>	69-0534
356	12.0 <sup>b</sup>	3.1	11.5	50	1.1	1.5 x 10 <sup>17</sup>	65-0483 <sup>d</sup>
423	25.2 <sup>b</sup>	4.4	33.0	50	1.1	1.5 x 10 <sup>17</sup>	65-0483 <sup>d</sup>
523	48.2 <sup>b</sup>	4.9	76.7	50	1.1	1.5 x 10 <sup>17</sup>	65-0483 <sup>d</sup>
583	61.0 <sup>b</sup>	5.5	100.0	50	1.1	1.5 x 10 <sup>17</sup>	65-0483 <sup>d,e</sup>
646	78.5 <sup>b</sup>	7.2	128.5	50	1.1	1.5 x 10 <sup>17</sup>	65-0483 <sup>d,e</sup>

a. Values calculated from residual yield of O<sub>2</sub> or NO after trapping at 77 K assuming 2NO + O<sub>2</sub> → 2NO<sub>2</sub>.

b. Values corrected assuming G(N<sub>2</sub>) = 10.0 at lowest temperature used.

c. Values calculated assuming reported residual yield of O<sub>2</sub> is due to incomplete trap reaction.

d. <sup>15</sup>N<sup>14</sup>NO was used in this work. The values given are the sums of the various isotopically labelled species.

e. Glass vessels used, in which thermal decomposition is negligible below 673 K (65-0483).

In one investigation (65-0483, see table 5.3.2) the isotopic distribution in the products from <sup>15</sup>N<sup>14</sup>NO was determined as a function of temperature.

With very high dose rate pulsed irradiation, the yields are independent of temperature up to 473 K (69-0013, table 5.3.3).

Since an increased decomposition of N<sub>2</sub>O with increasing temperature is not observed in the presence of SF<sub>6</sub> (69-0534) it appears that electron attachment is the primary process responsible

TABLE 5.3.2. Isotopic distribution in products from  $^{15}\text{N}^{14}\text{NO}$  at different temperatures

$^{28}\text{N}_2/\%$	7.8	15.0	10.0	10.3	9.6	10.7
$^{29}\text{N}_2/\%$	83.5	76.7	84.3	86.4	88.0	87.3
$^{30}\text{N}_2/\%$	8.7	8.3	5.7	3.3	2.4	2.0
$^{14}\text{NO}/\%$	68	65	60	56	54	54
$^{15}\text{NO}/\%$	32	35	40	44	46	46
Temperature/K	313	356	423	523	583	646
Reference = 65-0483		Pressure $\text{N}_2\text{O}$ = 50 torr				

for the temperature effect. Recently it has been suggested (72-0449) that electron detachment from  $\text{NO}^-$  (sec. 3.3) is more probable as a chain propagation step than the alternative suggested reaction:  $\text{NO}^- + \text{N}_2\text{O} \rightarrow \text{NO} + \text{N}_2 + \text{O}^-$  (65-0483).

TABLE 5.3.3. Dependence of yields on temperature (high dose rate pulsed irradiation)

$G(\text{N}_2)^a$	12.4	12.4	12.4	12.4	13.8	13.8	15.3	16.5	22.0	27.5
$G(\text{O}_2, \text{measured})^b$	2.0	2.0	2.0	2.0	1.5	0.7	0	0	0	0
T/K	298	323	398	473	540	573	623	673	723	773
	Values from 69-0013, fig. 1									
	$\text{N}_2\text{O}$ pressure = 760 torr									
	Total dose $0.6 - 4 \times 10^{20} \text{ eV g}^{-1}$									
	Dose rate = $10^{27} \text{ eV g}^{-1} \text{ s}^{-1}$									

- a. Values at temperature above 573 K were corrected for thermal decomposition of  $\text{N}_2\text{O}$ .  
 b. Yield measured as residual gas after trapping at 77 K.

#### 5.4. Electric Fields

The influence of D.C. electric fields on the course of  $\text{N}_2\text{O}$  radiolysis was studied in early work (see 48-0003 for references) and the application of this technique has been discussed in general terms (54-0009). Although its interpretation is rarely unambiguous, knowledge of how electric fields affect products can provide some information about the role of ion neutralization, of electron capture and of excitation by slow electrons in a radiolysis mechanism.

For a dose rate  $10^{13} \text{ eV g}^{-1} \text{ s}^{-1}$  and with 200 or 550 torr  $\text{N}_2\text{O}$ ,  $G(\text{N}_2)$  and  $G(\text{NO})$  increase with an increase in the ratio, applied field/ $\text{N}_2\text{O}$  pressure (X/P) in the region 1 to 7  $\text{V cm}^{-1} \text{ torr}^{-1}$ , i.e., where the ionization current is independent of X/P. A levelling off in the yields at about X/P = 5 was also reported although this effect is not apparent from the published results (58-0056). At 50 torr  $\text{N}_2\text{O}$ ,  $G(\text{N}_2)$  and  $G(\text{NO})$  decreased as X/P increased, the values passing through a minimum at X/P corresponding to the beginning of the plateau current region. At X/P higher than this,  $G(\text{N}_2)$  and  $G(\text{NO})$  increased with increasing X/P, in a manner similar to that at higher pressures. At all pressures studied,  $G(\text{O}_2)$  showed only a slight increase with X/P in the region where secondary ionization was negligible.

At a higher dose rate of  $10^{17} \text{ eV g}^{-1} \text{ s}^{-1}$  also,  $G(\text{N}_2)$  and  $G(\text{NO})$  increased with X/P (66-0434). The onset of the increase was the same for all  $\text{N}_2\text{O}$  pressures between 50 and 500 torr and occurred in the X/P region below that at which the ionization-current plateau was reached. The increase in yields with X/P continued throughout the plateau region, the extent of the increase being greater the lower the pressure.  $G(\text{O}_2)$  increased with X/P, but the increase was relatively small compared with that for the other products over most of the ionization current plateau region.

The results at the higher dose rate therefore show a qualitative resemblance in that  $G(\text{N}_2)$  and  $G(\text{NO})$  increase more markedly than  $G(\text{O}_2)$  at low X/P. The minimum in the  $\text{N}_2$  and  $\text{NO}$  yields found at the low dose rates was not apparent at the higher dose rates.

## 6. Effects of Additives on Yields

Although mechanistic information can often be obtained by the use of scavengers, in the case of  $N_2O$ , because of the large number of possible reactive intermediates and the rather poor understanding of how these react with particular additives, it is difficult to select specific scavengers. Relatively few scavenger studies have been reported and in no case has the investigation been detailed.

Tables 6.1 and 6.2 summarize the limited information available.

TABLE 6.1. Limiting yields with various additives (A) at room temperature

A	Conc. of A /mol percent	$G(N_2)$	$G(O_2)$	$G(NO)$	$P(N_2O)$ /torr	Ref.
$CCl_4$	0.4	$6.7 \pm 0.7$	1.2(0.12) <sup>a</sup>	—	800	69-0085
$CO_2$	7.5	$9.4 \pm 0.6^c$	$2.1 \pm 0.3^a$	—	800	69-0085
$CO_2$	3-8 <sup>e</sup>	$7.5 \pm 0.7$	$3.0 \pm 0.2^d$	$3.5 \pm 0.5^d$	200	70-0413
$NO^f$	0.25-8	$10 \pm 1^f$	—	—	50	65-0483
$H_2$	1-16	$10.0^f$	2.3(1) <sup>b,h</sup>	i	90, 380	61-0103
$H_2$	1-16	$10.0^f$	0.13(16) <sup>b,h</sup>	i	90, 380	61-0103
$C_2H_4$	2.3	$7.75^{f,j}$	—	—	50	65-0483
$CH_4$	6	$10.0^f$	0 <sup>h</sup>	—	380	61-0103
$SF_6$	0.1-1.0	$6.7^{f,m}$	—	—	800	69-0534
$SF_6$	0.12-1.0	$7.25 \pm 0.6$	$1.8 \pm 0.5^a$	—	800	69-0085
$SF_6$	0.01-0.2	8.0	$3.2^d$	$3.1^d$	200	70-0413
$SF_6$	0.3-5 <sup>l</sup>	$8.2 \pm 0.3^k$	—	—	700	69-0369

Yields in absence of additives (cf. tables 4.1-4.3):

$$G(N_2) = 10.0$$

$$G(O_2, \text{ measured}) = 2.0 \text{ (residual yield after trapping at 77 K).}$$

$$G(O_2) = 4.0$$

- a. Residual  $O_2$  after trapping at 77 K.  
b.  $G$  dependent on additive concentration; values are for the extremes of the scavenger concentration used, these being given in parentheses (mol percent).  
c. Compare  $G(N_2) = 9.9 \pm 0.5$  obtained in the absence of scavenger.  
d. Yields are those calculated by the author from the residual yield after trapping at 77 K and were corrected for the contribution from the energy absorbed by the scavenger.  
e. Below 3 mol percent  $CO_2$ , the  $G$ -values of the products increased with decreasing  $CO_2$  concentration.  
f. Calculated assuming  $G(N_2) = 10$  in the absence of scavenger.  
g.  $^{15}NO$  used as scavenger in  $^{14}N^{14}NO$  and  $^{15}N^{14}NO$ . Given  $G(N_2)$  is total  $N_2$ . For yields of isotopically labelled products see table 6.2.  
h. Given values measured by direct gas chromatography of products.  
i.  $G(NO, \text{ measured})$  decreased with increasing  $H_2$  concentration but appeared to reach a limiting value of 1.3 at  $H_2$  concentration greater than 5 mol percent.  
j.  $G(N_2)$  increased with temperature to 10.9 and 23.9 at 423 and 548 K respectively.  
k. Very high dose rate ( $10^{27}eV g^{-1}s^{-1}$ ) pulsed irradiation.  
l.  $G(N_2)$  increased with decreasing  $SF_6$  below ca. 0.3 mol percent.  
m. With 0.1 mol percent  $SF_6$  present  $G(N_2)$  was essentially independent of temperature up to 473 K.

TABLE 6.2. Isotopically labelled products from  $N_2O$  with  $^{15}NO$  present (65-0483)

$G(N_2)$	10	11.16	10.55	10	9.96	10.0	10.5
$G(^{29}N_2)$	10	10.6	8.4	0.78	1.14	1.56	2.0
$G(^{29}N_2)$	—	0.16	1.8	8.35	8.1	8.0	8.0
$G(^{30}N_2)$	—	0.4	0.35	0.87	0.72	0.55	0.48
$G(^{14}NO)$	2.15	7.6	—	—	—	—	—
$N_2O$	$^{14}N^{14}NO$	$^{14}N^{14}NO$	$^{14}N^{14}NO$	$^{15}N^{14}NO$	$^{15}N^{14}NO$	$^{15}N^{14}NO$	$^{15}N^{14}NO$
$^{15}NO$ conc. (mol percent)	0	0.25	5.7	0	1.6	7.9	26.0

Values corrected assuming  $G(N_2) = 10.0$  in absence of  $NO$ .

## 7. Rare Gas Sensitized Radiolysis

Only one study of the yields from rare gas - N<sub>2</sub>O mixtures has been reported (70-0413). Products were formed from N<sub>2</sub>O as a consequence of energy absorption in the rare gas fraction of the mixture.

Difficulties arise in quantitative assessment of the data from this type of experiment since determination of the yield due to the energy absorbed by the rare gas,  $G(\text{product, sensitized})$ , requires knowledge of (a) the partition of total absorbed energy between the components of the mixture and (b) the effect of the rare gas on the yield due to the energy absorbed by the N<sub>2</sub>O fraction of the mixture,  $G(\text{product, N}_2\text{O})$ .

In the work reported (70-0413) it was assumed that the fraction of the total energy absorbed by each component was equal to its electron fraction in the mixture (see 68-8036 for discussion of the validity of the assumption). Results obtained with constant N<sub>2</sub>O pressure and varying rare gas pressure indicated that  $G(\text{product, N}_2\text{O})$  in the mixtures was the same as in pure N<sub>2</sub>O.

Values obtained for  $G(\text{product, sensitized})$  are given in table 7. These should be regarded as tentative in view of the assumptions made in their calculation.

TABLE 7. Rare gas sensitized radiolysis of N<sub>2</sub>O (70-0413)

$G(\text{N}_2)$	7.3	6.3	3.0	2.9	3.8
$G(\text{O}_2)$	2.8	2.4	1.5	1.6	1.8
$G(\text{NO})$	3.0	3.2	0.0	0.5	0.5
$G(-\text{N}_2\text{O})$	8.8	7.9	3.0	3.2	4.1
Sensitizing Gas	He	Ne	Ar	Kr	Xe

Reported yields are those attributable to energy absorbed in the rare gas fraction of the mixture. It is assumed that energy partition in gas mixtures is according to electron density.  $G$  values obtained from slope of plot of (total yield of product/energy absorbed by N<sub>2</sub>O fraction) against the ratio of the partial pressures  $P(\text{rare gas})/P(\text{N}_2\text{O})$ . Those plots were linear (for mixtures with constant  $P(\text{N}_2\text{O})=50$  torr) for all products using He and Ne, for all products except NO using Kr and Ar. Linearity was not observed for any of the products using Xe.

$G(\text{O}_2)$  and  $G(\text{NO})$  calculated from residual gas yield after trapping at 77 K, assuming  $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ .

## 8. N<sub>2</sub>O as Additive

One of the main uses of N<sub>2</sub>O in radiation chemistry has been as a selective scavenger for electrons. In the gas phase, N<sub>2</sub>O was first used for this purpose in studies of hydrocarbon radiolysis (65-0431). When it is present at scavenger concentrations, the radiation chemistry of N<sub>2</sub>O is simplified compared with that of pure N<sub>2</sub>O, and studies of N<sub>2</sub>O can give information about some of its reactions, particularly electron capture and the subsequent negative ion reactions.

Information relevant to N<sub>2</sub>O radiolysis obtained in studies involving N<sub>2</sub>O as scavenger is summarized in tables 8.1 and 8.2. The effects of N<sub>2</sub>O on the products from the system are not included.  $G(\text{N}_2)$  is the yield due to energy absorption by the main components of the system. Except where stated,  $G(\text{N}_2)$  is independent of N<sub>2</sub>O concentration above the given N<sub>2</sub>O concentration. The "second additive" column lists compounds added to the main system to investigate their effect on  $G(\text{N}_2)$ . Some information about such effects is given in the comments; for full details the references should be consulted.

TABLE 8.1.  $G(N_2)$  from gases containing  $N_2O$  as additive (organic systems)

System	$G(N_2)$	Conc. $N_2O$ /mol percent	Other Additives	$10^{-15}$ ·Dose Rate /eV $g^{-1}s^{-1}$	$10^{-19}$ ·Max. Total Dose /eV $g^{-1}$	Ref.	Note
ethane	6.5	2	$CO_2$ , $SF_6$ , alkenes	16	16	67-0247	a
propane	7.2	2	$SF_6$ , $CCl_4$ , $C_3H_6$	5.0	3.0	65-0431	a
propane	6.5	2	alcohols	16	16	68-0005	a,b
propane	6.5	2	$H_2O$ , $NH_3$ , $CHCl_3$	10	3.0	69-0294	c
butane	6.5	2	$CO_2$ , $SF_6$ , alkenes	8.3	8.3	67-0247	a
butane	6.5	2	alcohols	8.3	8.3	68-0005	a,b
iso-butane	6.5	2	alcohols	8.3	8.3	68-0005	a,b
propylene	4.2	2	—	11	1.1	68 0005	a
iso-butylene	4.2	2	—	8.3	8.3	68-0005	a
cis-2-butene	8.4	2	$CO_2$	8.3	8.3	68-0005	a
trans-2-butene	8.4	2	$SF_6$	8.3	8.3	68-0005	a
cyclohexane	11.5	2	$SF_6$	8.2	2.2	68-0506	a
benzene	13.3	10	—	34	4.5	68-0043	d
benzene	24.9	3	$SF_6$ , $CO_2$	4.1	9.1	68-0230	d
methanol	48	6.5	—	0.38	9.0	65-0432	e
methanol	< 0.1	1	—	$5 \times 10^8$	0.5	64-0154	f

- a.  $N_2$  formation attributed to dissociative electron capture by  $N_2O$ . Subsequent negative ion reactions are discussed.  
b. Effect of MeOH, EtOH and 2-PrOH on secondary negative ions is discussed.  
c. Temperature dependence of  $G(N_2)$  studied. Effects of second additives attributed to negative ion clustering.  
d.  $G(N_2)$  dependent on  $N_2O$  conc. and dose rate. Value given is the maximum observed. Chain mechanism involving  $O^-$  suggested by authors.  
e. Chain reaction indicated.  
f. High dose-rate pulse irradiation.

TABLE 8.2.  $G(N_2)$  from gases containing  $N_2O$  as additive (inorganic systems)

System	$G(N_2)$	$N_2O$ /mol percent	Other Additives	$10^{-16}$ ·Dose Rate /eV $g^{-1}s^{-1}$	$10^{-19}$ ·Max. Total Dose /eV $g^{-1}$	Ref.	Note
$H_2O$	3.8	> 0.1	—	not stated	1.0	65-0005	a
$H_2O$	3.5	3	$SF_6$ , $C_3H_6$ , $C_6H_6$	0.5	3.0	67-0093	b
$H_2O$	3.0	3	—	3.0	12	68-0112	
$NH_3(+C_3H_8)$	3.8	1.5	$SF_6$ , $C_3H_8$	1.4	6.0	68-0659	c
$^{30}N_2$	2.9	1.4	—	1.7	6.0	65-0791	d

- a. Dosimetry not stated.  
b. Values corrected to  $G(N_2) = 10$  in  $N_2O$  dosimeter.  
c. High  $G(N_2)$  in absence of  $C_3H_8$  indicated chain reaction leading to  $N_2$ .  
d. System irradiated was  $^{30}N_2 + ^{28}N_2O$ .  $G(^{28}N_2)$  decreased with increasing  $N_2O$  concentration. Given value is extrapolated to zero  $N_2O$  concentration.

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## 9. References

- 19-0001 Chemical actions of radiation.  
Wourtsel, E.  
LE RADIUM 11: 289-98 and 332-47 (1919).
- 48-0003 The effect of electric fields on the decomposition of nitrous oxide by alpha-rays.  
Williams, N.T.; Essex, H.  
J. CHEM. PHYS. 16(12): 1153-7 (1948).
- 53-9004 Absorption coefficients of gases in the vacuum ultraviolet. Part II. Nitrous oxide.  
Zelikoff, M.; Watanabe, K.; Inn, E.C.Y.  
J. CHEM. PHYS. 21(10): 1642-7 (1953).
- 54-0009 The mechanism of gas phase radiation-chemical reactions.  
Essex, H.  
J. PHYS. CHEM. 58(1): 42-9 (1954).
- 56-0023 Nitrous oxide dosimeter for high levels of betas, gammas, and thermal neutrons.  
Harteck, P.; Dondes, S.  
NUCLEONICS 14(3): 66-72 (1956).
- 56-0024 Ionization chambers.  
Boag, J.W.  
Radiation Dosimetry, Hine, G.J. and Brownell, G.L. (eds.), Academic Press, New York, 1956, p. 153-212.
- 57-7006 Rate constants at low concentrations. III. Atomic oxygen reactions in the photolysis of nitrogen dioxide at 3600 Å.  
Ford, H.W.; Endow, N.  
J. CHEM. PHYS. 27(5): 1156-60 (1957).
- 57-9008 Reactions of nitrogen atoms. I. Oxygen and oxides of nitrogen.  
Kistiakowsky, G.B.; Volpi, G.G.  
J. CHEM. PHYS. 27(5): 1141-9 (1957).
- 58-0056 The x-ray decomposition of nitrous oxide.  
Burt, B.P.; Kircher, J.F.  
RADIATION RES. 9: 1-12 (1958).
- 60-0107 A radiation-induced chain reaction in the decomposition of nitrous oxide.  
Johnson, G.R.A.  
PROC. CHEM. SOC.: 213-4 (1960).
- 60-0119 Gamma irradiation experiments in the N<sub>2</sub>-O<sub>2</sub> system. Report No. 1 on radiation processing.  
Steinberg, M.  
BNL-612, June, 1960, 20p.
- 61-0103 Nitrous oxide as a dosimeter for ionizing radiations.  
Hearne, J.A.; Hummel, R.W.  
RADIATION RES. 15: 254-67 (1961).
- 62-0146 The nitrous oxide radiation dosimeter.  
Johnson, G.R.A.  
J. INORG. NUCL. CHEM. 24: 461-8 (1962).
- 62-9017 Bond Energies, Ionization Potentials and Electron Affinities.  
Vedeneyev, V.I.; Gurvich, L.V.; Kondrat'yev, V.N.; Medvedev, V.A.; Frankevich, Ye.L.  
St. Martin's Press, New York, 1966, 202p.
- 63-0195 High-dose N<sub>2</sub>O dosimeter.  
Flory, D.A.  
NUCLEONICS 21(12): 50-4 (1963).
- 64-0154 Production of hydrogen in the radiolysis of methanol vapour.  
Meaburn, G.M.; Mellows, F.W.; Reiffsteck, A.  
NATURE (LONDON) 204: 1301-2 (1964).
- 64-0177 Gas-phase dosimetry by use of ionization measurements.  
Meisels, G.G.  
J. CHEM. PHYS. 41(1): 51-6 (1964).
- 64-7008 Vacuum ultraviolet photochemistry.  
McNesby, J.H.; Okabe, H.  
ADVAN. PHOTOCHEM. 3: 157-240 (1964).
- 64-9020 Negative-ion-molecule reactions in nitrous oxide.  
Burt, B.P.; Henis, J.  
J. CHEM. PHYS. 41(5): 1510-1 (1964).
- 64-9021 Mass-spectrometric study of the reactions of O atoms with NO and NO<sub>2</sub>.  
Klein, F.S.; Herron, J.T.  
J. CHEM. PHYS. 41(5): 1285-90 (1964).  
Erratum: J. CHEM. PHYS. 44: 3645-6 (1966).
- 65-0005 Electron yield in the γ-radiolysis of water vapor.  
Baxendale, J.H.; Gilbert, G.P.  
SCIENCE 147: 1571 (1965).
- 65-0431 Effect of electron scavengers on the formation of hydrogen in the radiolysis of propane.  
Johnson, G.R.A.; Warman, J.M.  
TRANS. FARADAY SOC. 61: 1709-14 (1965).
- 65-0432 Effect of hydrogen atom and electron scavengers on the radiolysis of methanol vapour.  
Meaburn, M.; Mellows, F.W.  
TRANS. FARADAY SOC. 61: 1701-8 (1965).
- 65-0483 Radiolysis of N<sup>15</sup>N<sup>14</sup>O.  
Gordon, R.; Ausloos, P.  
J. RES. NAT. BUR. STD. 69A: 79-85 (1965).
- 65-0791 Isotopic exchange in nitrogen gas induced by γ-radiation.  
Dawes, D.H.; Back, R.A.  
J. PHYS. CHEM. 69(7): 2385-92 (1965).
- 66-0312 A practical comparison between nitrous oxide dosimetry and Fricke dosimetry for the estimation of γ-ray energy absorbed in gaseous media.  
Furukawa, K.; Shida, S.  
J. NUCL. SCI. TECHNOL. (TOKYO) 3(1): 41-2 (1966).
- 66-0434 Nitrous oxide dosimetry. Effects of temperature, pressure, and electric field.  
Jones, F.T.; Sworski, T.J.  
J. PHYS. CHEM. 70(5): 1546-52 (1966).
- 66-9042 Some negative ion reactions in simple gases.  
Paulson, J.F.  
ADVAN. CHEM. SER. 58: 28-43 (1966).
- 66-9163 Compilation of Mass Spectral Data.  
Cornu, A.; Massot, R.  
Heyden and Son Ltd., London, 1966, 323p.
- 67-0093 Primary processes in the formation of hydrogen atoms in the radiolysis of water vapor.  
Johnson, G.R.A.; Simic, M.  
J. PHYS. CHEM. 71(4): 1118-23 (1967).
- 67-0247 Electron capture by nitrous oxide in irradiated alkane and alkene gases. Subsequent reactions of the O<sup>-</sup> ion.  
Warman, J.M.  
J. PHYS. CHEM. 71(12): 4066-72 (1967).
- 67-9124 N<sub>2</sub>O bond dissociation energy.  
Kaufman, F.  
J. CHEM. PHYS. 46(6): 2449 (1967).
- 67-9126 Reactions of nitrogen atoms in the gas phase.

- Brocklehurst, B.; Jennings, K.R.  
 PROG. REACTION KINETICS 4: 1-36 (1967).
- 67-9127 Kinetic behavior of  $N_2(A^3\Sigma_u^+)$  in active nitrogen.  
 Thrush, B.A.  
 J. CHEM. PHYS. 47(9): 3691 (1967).
- 67-9129 Study of collision-induced phenomena with a Dempster mass spectrometer.  
 Harris, H.H.; Russell, M.E.  
 J. CHEM. PHYS. 47(7): 2270-5 (1967).
- 68-0005 The reaction of  $O^-$  with alcohols in gas-phase radiolysis.  
 Warman, J.M.  
 J. PHYS. CHEM. 72(1): 52-6 (1968).
- 68-0043 Gas-phase radiolysis of benzene.  
 Hentz, R.R.; Rzad, S.J.  
 J. PHYS. CHEM. 72(3): 1027-31 (1968).
- 68-0112 Effects of electron scavengers in the radiolysis of water vapor.  
 Dixon, R.S.; Bailey, M.G.  
 CAN. J. CHEM. 46(8): 1181-6 (1968).
- 68-0230 The formation of phenol and nitrogen by a negative ion-molecule chain reaction on irradiation of gaseous benzene-nitrous oxide mixtures.  
 Rzad, S.J.; Warman, J.M.  
 J. PHYS. CHEM. 72(8): 3013-7 (1968).
- 68-0318 The dosimetry of very high intensity pulsed electron sources used for radiation chemistry: II. Dosimetry for gaseous samples.  
 Willis, C.; Miller, O.A.; Rothwell, A.E.; Boyd, A.W.  
 ADVAN. CHEM. SER. 81: 539-49 (1968).
- 68-0506  $\gamma$ -Radiolysis of cyclohexane with electron scavengers. VI.  $N_2O$  and  $SF_6$  as electron scavengers in the vapor phase.  
 Sagert, N.H.; Robinson, R.W.; Blair, A.S.  
 CAN. J. CHEM. 46(22): 3511-6 (1968).
- 68-0659 Primary processes in the radiolysis of gaseous ammonia.  
 Johnson, G.R.A.; Simic, M.  
 ADVAN. CHEM. SER. 82: 197-211 (1968).
- 68-7198 Vacuum-ultraviolet photolysis of  $N_2O$ . I. Metastable species produced at 1470 Å.  
 Young, R.A.; Black, G.; Slanger, T.G.  
 J. CHEM. PHYS. 49(11): 4769-76 (1968).
- 68-8036 Energy deposition mechanisms.  
 Klots, C.E.  
 Fundamental Processes in Radiation Chemistry, Ausloos, P.(ed.), Interscience Publishers, New York, 1968, p.1-57.
- 68-9042 Three-body electron capture by nitrous oxide.  
 Warman, J.M.; Fessenden, R.W.  
 J. CHEM. PHYS. 49(10): 4718-9 (1968).
- 68-9063 Gas phase reaction kinetics of neutral oxygen species.  
 Johnston, H.S.  
 NSRDS-NBS-20, Sept., 1968, 49p.
- 68-9071 Negative-ion-molecule reactions in  $N_2O$ .  
 Moruzzi, J.L.; Dakin, J.T.  
 J. CHEM. PHYS. 49(11): 5000-6 (1968).
- 68-9078 Electron attachment in  $N_2O$ .  
 Phelps, A.V.; Voshall, R.E.  
 J. CHEM. PHYS. 49 (7): 3246-8 (1968).
- 69-0013 Effect of temperature on yields in the radiolysis of nitrous oxide with high intensity electron pulses.  
 Boyd, A.W.; Willis, C.; Miller, O.A.  
 CAN. J. CHEM. 47(2): 351-2 (1968).
- 69-0085 Effect of density and electron scavengers in nitrous oxide radiolysis.  
 Sears, J.T.  
 J. PHYS. CHEM. 73(4): 1143-46 (1969).
- 69-0294 Effect of polar molecules on reaction of negative ions in radiolysis of hydrocarbon + nitrous oxide systems in the gas phase.  
 Redpath, J.L.; Simic, M.  
 J. PHYS. CHEM. 73(9): 2809-14 (1969).
- 69-0369 Gas phase radiolysis of hydrogen chloride, hydrogen bromide, and nitrous oxide with intense electron pulses.  
 Willis, C.; Boyd, A.W.; Armstrong, D.A.  
 CAN. J. CHEM. 47: 3783-91 (1969).
- 69-0534 Ionic processes in the radiolysis of nitrous oxide.  
 Hummel, R.W.  
 CHEM. COMMUN. (17): 995-6 (1969).
- 69-6025 Vacuum-ultraviolet photolysis of  $N_2O$ . IV. Deactivation of  $N(^2D)$ .  
 Black, G.; Slanger, T.G.; St. John, G.A.; Young, R.A.  
 J. CHEM. PHYS. 51(1): 116-21 (1969)
- 69-7003 Vacuum-ultraviolet photolysis of  $N_2O$ . II. Deactivation of  $N_2(A^3\Sigma_u^+)$  and  $N_2(B^3\Pi_g)$ .  
 Young, R.A.; Black, G.; Slanger, T.G.  
 J. CHEM. PHYS. 50(1): 303-8 (1969).
- 69-9031 Electron attachment to  $N_2O$ .  
 Chaney, E.L.; Christophorou, L.G.  
 J. CHEM. PHYS. 51(3): 883-92 (1969).
- 69-9080 Critical evaluation of rate data for homogeneous, gas phase reactions of interest in high-temperature systems.  
 Baulch, D.L.; Drysdale, D.D.; Horne, D.G.; Lloyd, A.C.  
 High Temperature Reaction Rate Data, No.4, Dec., 1969, 63p.
- 69-9129 Temperature dependence of dissociative attachment in  $N_2O^+$ .  
 Chantry, P.J.  
 J. CHEM. PHYS. 51(8): 3369-79 (1969).
- 69-9135 Negative ion-molecule reactions.  
 Ferguson, E.E.  
 CAN. J. CHEM. 47: 1815-20 (1969).
- 69-9136 Negative ions of  $N_2O$  and  $CO_2$ .  
 Bardsley, J.N.  
 J. CHEM. PHYS. 51(8): 3384-9 (1969).
- 70-0046 Ion neutralization reactions in irradiated hydrogen chloride, hydrogen bromide, and nitrous oxide.  
 Wilson, D.E.; Armstrong, D.A.  
 CAN. J. CHEM. 48(4): 598-602 (1970).
- 70-0239 The radiolysis of alcohols.  
 Freeman, G.R.  
 ACTIONS CHIM. BIOL. RADIATIONS 14: 73-134 (1970)
- 70-0384 Low pressure radiolysis of  $N_2O$ .  
 Bakale, G.; Fessenden, R.W.; Warman, J.M.  
 160th Meeting of the Am. Chem. Soc., Div. Phys. Chem., Chicago, Ill., Sept. 14-8, 1970, Abstr. No. 123.
- 70-0413 Ionic processes in the radiolysis of nitrous oxide. The effect of electron scavenger and rare gas sensitization.  
 Takao, S.; Shida, S.  
 BULL. CHEM. SOC. JAPAN 43(9): 2766-71 (1970).
- 70-7558 Reaction of  $O(^1D)$  with  $N_2O$ .  
 Greenberg, R.I.; Heicklen, J.  
 INT. J. CHEM. KINETICS 2: 185-9 (1970).
- 70-9074 Ion Molecule Reactions.



- McDaniel, E.W.; Cermak, V.; Dalgarno, A.; Ferguson, E.E.; Friedman, L.  
Wiley-Interscience, New York, 1970, 374p.
- 70-9229 Negative-ion-neutral reactions in N<sub>2</sub>O.  
Paulson, J.F.  
J. CHEM. PHYS. 52(2): 959-62 (1970).
- 71-0199 The absolute dosimetry of high intensity 600 kV pulsed electron accelerator used for radiation chemistry studies of gaseous samples.  
Willis, C.; Boyd, A.W.; Miller, O.A.  
RADIAT. RES. 46: 428-43 (1971).
- 71-7181 The photolysis of N<sub>2</sub>O at 1470 Å.  
Dodge, M.C.; Heicklen, J.  
INT. J. CHEM. KINET. 3(3): 269-82 (1971).
- 71-7213 The reaction of the electronically excited oxygen atom O(<sup>1</sup>D<sub>2</sub>) with nitrous oxide.  
Scott, P.M.; Preston, K.F.; Andersen, R.J.; Quick, L.M.  
CAN. J. CHEM. 49(11): 1808-17 (1971).
- 71-9364 Threshold electron impact excitation spectra. IV. Triatomic molecules nitrous oxide, carbon dioxide, carbonyl sulfide, and carbon disulfide.  
Hubin-Franskin, M.J.; Collin, J.E.  
BULL. SOC. ROY. SCI. LIEGE 40(5-8): 361-84 (1971).
- 72-0088 Primary yields and mechanisms in the radiolysis of N<sub>2</sub>O from high intensity electron pulse irradiations of N<sub>2</sub>O-O<sub>2</sub> mixtures.  
Willis, C.; Boyd, A.W.; Bindner, P.E.  
CAN. J. CHEM. 50(10): 1557-67 (1972).
- 72-0449 Dissociative attachment of thermal electrons to N<sub>2</sub>O and subsequent electron detachment.  
Warman, J.M.; Fessenden, R.W.; Bakale, C.  
J. CHEM. PHYS. 57(7): 2702-11 (1972).
- 72-9150 Electron attachment and negative ion molecule reactions in nitrous oxide.  
Parkes, D.A.  
J. CHEM. SOC. FARADAY TRANS. I 68(11): 2103-20 (1972).