The Radiation Chemistry of Gaseous Ammonia

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NSRDS

Foreword

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RICHARD W. ROBERTS, *Director*

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H_2 and N_2 are the only significant products of radiolysis of gaseous ammonia under static conditions at dose rates less than about $10^{19} eV \cdot g^{-1} s^{-1}$; and $G(H_2) = 5.0 \pm 1.0$ and $G(N_2) = 1.7 \pm 0.3$ for irradiation at 20°C and pressures near one atmosphere. Yields do not appear to depend significantly upon LET (linear energy transfer); and they are independent of dose up to at least $8 \times 10^{22} eV/g$. In static systems at dose rates $\geqslant 10^{26} eV \cdot g^{-1} s^{-1}$, and in flow systems, N_2H_4 is also a product.

At dose rates less than $10^{19} eV \cdot g^{-1} s^{-1}$, $G(-NH_3)$ increases markedly with temperature and reaches a plateau value of about 10 at temperatures near $150 - 200$°C. At very high dose rates ($\geqslant 10^{26} eV \cdot g^{-1} s^{-1}$) $G(-NH_3)$ increases significantly at higher temperatures (value depends upon dose rate) and $G(-NH_3)$ does not appear to be leveling off at the highest temperature studied (460°C). In both dose rate regions the increase in $G(-NH_3)$ is attributed primarily to the increasing importance of $NH_3 + H \rightarrow NH_2 + H_2$ with increasing temperature. $G(-NH_3)$ also appears to increase with decreasing dose rate. However, the effect is less pronounced than the effect of temperature, and the experimental evidence is not unequivocal.

NH and NH_2 have been observed spectroscopically in pulse radiolysis of NH_3 and such studies lead to $g(NH) = 0.4$. However, this value of $g(NH)$ is low because of errors in dosimetry. $g(NH_2)$ was not obtained directly because the absorptivity of NH_2 was not available. A number of additives has been employed in attempts to determine primary yields of other species involved in radiolysis; however, results with different additives and from different laboratories are in good agreement only in the case of $g(H_2)$ $(0.7 - 0.8)$ and $g(NH_4^+)$ $(3.3 - 3.9)$. The best value of $g(H)$ appears to be 10.4 ± 0.6; and this is the preferred value. $g(NH_2)$ is obtained from the material balance, $g(H) + 2g(H_2) = g(NH_2) + 2g(NH)$. The preferred value of $g(NH)$ is 0.75, i.e., $g(NH) = g(H_2)$ and this leads to $g(NH_2) = 10.4$.

Key words: Ammonia; chemical kinetics; data compilation; G; g; gas; radiation chemistry; rates; review.

1. Introduction

This compendium provides a comprehensive summary of data relevant to the radiation chemistry of gaseous ammonia. A complete mechanism for the radiolysis of ammonia cannot be written at present. However, probable contributing processes are discussed in some detail and the supporting evidence is examined critically when possible. Specific rates and/or energies of activation for these elementary processes are given when available but in general such data are not critically evaluated. Properties such as bond energies, ionization energies and electron affinities are tabulated for the major intermediates (app. 1). Such data have for the most part been taken from authoritative reference sources and are presented without critical comment. Preferred values are given for yields of both products (sec. 3) and intermediates (sec. 2.2.1 and 2.2.2).

Throughout the text and tables references are cited by Radiation Chemistry Data Center serial number; in many cases, the authors, or first author only, are included with serial number for easy identification of the work. When only a first author is cited, that name is followed by periods corresponding to the number of co-authors, as Nishikawa..68–0505. The bibliography is a listing of references by serial number; the first two digits of the number represent the year, so that the

Table 2.1. *Elementary processes*

| Reaction	Specific rate[a]	Comments
(1) $NH_3 \xrightarrow{} NH_3^+ + e^-$ $\xrightarrow{} NH_2^+ + H + e^-$ $\xrightarrow{} NH^+ + H_2 + e^-$	—	Accounts for $\sim 97\%$ of total ionization at 2×10^{-7} torr for 100 eV e^-; relative abundances are $NH_3^+ : NH_2^+ : NH^+ = 100.0 : 40.9 : 4.5$ (66–0298).
(2) $NH_3 \xrightarrow{} NH_3^*$	—	NH_3^* represents totality of electronically excited states produced.
(3) $NH_3^* \rightarrow NH_2 + H$	—	Only primary process in photolysis when $\lambda > 160$ nm (69–7017, 68–7168, 62–7002, 62–0132). NH_2 has been obs. spectrophotometrically in pulsed radiolysis (71–0169).
(4) $NH_3^* \rightarrow NH + H_2$ (5) $NH_3^* \rightarrow NH + 2H$	— —	In photolysis (4) accounts for about 12% of primary dissociation 147 nm[b] (64–7003) and 14% at 123.6 nm[b] (62–0132). $g(4) \cong 0.64^c$ (68–0051). NH observed spectrosocopically in pulse radiolysis; $g(NH) \cong 0.4$ (68–0101). Also observed spectroscopically in photochemistry at $\lambda < 160$ nm (67–7484, 63–6002, 63–0149, 62–7002).
(6) $NH_3^* + NH_3 \rightarrow 2NH_3$	—	Importance of (6) depends upon lifetime of excited state. Spectral and photochemical evidence indicates that excitation between 217 and 166 nm leads to predissociation (35–9001, 64–7008).
(7) $NH_3^+ + NH_3 \rightarrow NH_4^+ + NH_2$	$6–11 \times 10^{11}$ [d]	k_7 decreases with increasing translational energy of ion (70–0563).
(8) $NH_2^+ + NH_3 \rightarrow NH_3^+ + NH_2$	1.1×10^{11} (66–0298, 63–0150); 2.4×10^{11} (70–0563)	—
(9) $NH_2^+ + NH_3 \rightarrow NH_4^+ + NH$	3.9×10^{11} (66–9068, 67–9079); 6.5×10^{11} (70–0563)	k_8/k_9 depends upon translational energy of ion (70–0563).
(10) $NH^+ + NH_3 \rightarrow N_2H_2^+ + H_2$	1.8×10^9 (66–0298)[e]	—
(11) $NH_4^+ + e^- \rightarrow NH_3 + H$	$(1.5 \pm 0.3) \times 10^{16}$ (71–0002). (See also 66–0201).	$g(NH_4^+) \cong 3.9$ estimated from studies with SF_6 as additive[f]. NH_4^+ accounts for $\sim 99\%$ of + ions at 1 torr in radiolysis with 100 eV e^- (66–0298).
(12) $NH_4^+ + e^- \rightarrow NH_2 + H_2$	—	Limiting value of $G(H_2)$ in presence of H–scavengers leads to *upper limit* of ~ 0.8 for $g(12)^g$. Studies with CCl_4 indicate $g(12) \cong 0.1^h$.
(12') $NH_4^+ + e^- \rightarrow NH_2 + 2H$	—	At normal temperatures and pressures (12') is endothermic by ~ 40 kcal because of solvation of NH_4^+ (69–0326, 67–0546).
(13) $NH_2 + H + M \rightarrow NH_3 + M$	$\sim 1.2 \times 10^{10}$ (63–9010)[e] 1.8×10^{10} (71–0216)[f] 1.2×10^{11} (71–0169)	Pseudo–second order > 1000 torr (71–0169).
(13') $NH_2 + H \rightarrow NH + H_2$	$\sim 2.9 \times 10^9$ (71–0216)[f]	Exothermic by 14 kcal.
(14) $NH_2 + NH_2 + (M) \rightarrow N_2H_4 + (M)$	$\sim 2.5 \times 10^9$ (64–7002)[i] $\sim 1.8 \times 10^9$ (71–0216)[f]	Pseudo–second order above ~ 0.45 torr (63–9010). N_2H_4 is significant product in flow systems (67–0271) and in static systems at $\geq 10^{20}$ eV·g^{-1}s^{-1} (68–0101, 69–0272) See also 71–0169.
(15) $NH_2 + NH_2 \rightarrow NH + NH_3$	4.6×10^8 (64–7002)[i,j]; 5×10^8 (71–0216)[f]	—
(16) $NH_2 + N_2H_4 \rightarrow NH_3 + N_2H_3$	$10^9 \exp(-7,000/RT)$ (65–9044)[k]	—
(16') $NH_2 + H_2 \rightarrow NH_3 + H$	—	Endothermic by 0.1 kcal. Failure to observe dose dependence indicates (16') unimportant under usual conditions (see section 3.2.1).
(17) $NH + NH_3 \rightarrow N_2H_4$	1.0×10^{10} (68–7214)[l]	—
(17') $NH + NH_3 \rightarrow 2 NH_2$	—	Exothermic by 14 kcal.

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Photochemical studies indicate that (3) is

$$(3) \ NH_3* \rightarrow NH_2 + H$$
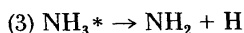
the only dissociation process at wavelengths greater than 160 nm (ref. in table 2.1). At shorter wavelengths (4) and (5) also occur, however reactions (3) and (5) account for 80% of the dissociation.

$$(4) \ NH_3* \rightarrow NH + H_2$$
$$(5) \ NH_3* \rightarrow NH + 2H$$
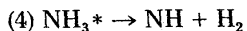
The spectra of both NH_2 (71–0169) and NH (68–0101) have been observed in pulsed radiolysis. Primary positive ions from (1) undergo rapid ion–molecule reactions (7) − (10) and are thereby converted almost exclusively to NH_4^+ (66–0298). The relative importance of possible modes of neutralization of NH_4^+ (11), (12), and (12′) has been investigated by addition of electron scavengers. In pure ammonia, NH_4^+ is neutralized by e^- since negative ion formation is negligible (66–0298, 34–9002). In the presence of electron scavengers, NH_4^+ is neutralized by the negative ion formed in the scavenging process.

Nishikawa and co–workers (67–0263, 68–0051) have studied the system $NH_3 - CCl_4$. They assume CCl_4 scavenges electrons in a dissociative attachment that leads to CCl_3 and Cl^-, and that neutralization of NH_4^+ with Cl^- yields NH_4Cl. Because CCl_4 also scavenges H atoms, the limiting value of $G(H_2)$ in the presence of CCl_4 should be the primary yield of non–scavengable H_2 from processes other than (12).

$$(12) \ NH_4^+ + e^- \rightarrow NH_2 + H_2$$
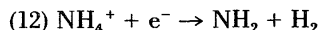
Comparison of this limiting yield of 0.64 with the total non–radical yield of 0.75 (see table 3.2.1) leads to the conclusion that $g(12) \sim 0.1$.

Neutralization of NH_4^+ to give NH_2 and 2H (12′) is endothermic by about 40 kcal (69–0326, 67–0546) if, as seems reasonable, NH_4^+ is solvated at normal temperature and pressures (68–0032, 66–9067, 64–9015). Thus, it appears that neutralization of NH_4^+ in pure ammonia proceeds almost exclusively by reaction (11). In support of such a conclusion, Gordon, Mulac, and Nangia (71–0169) have found that the initial concentration of NH_2 measured spectrophotometrically, is unchanged when SF_6 is added to NH_3.

Gordon, Mulac and Nangia (71–0169) also conclude from the comparison of results for pure NH_3 and $NH_3 - SF_6$ that 45 percent of the hydrogen atoms are produced by ion–neutralization as opposed to dissociation of excited states. This can be compared with the results of Nishikawa and co-workers (67–0263, 68–0051) who reported that approximately 42 percent of the hydrogen (H_2) is the result of ion–neutralization. The latter estimate is based upon a comparison of hydrogen yields from NH_3 and $NH_3 - N_2O$. It is assumed that ion–neutralization does not produce hydrogen atoms in the presence of N_2O; and thus, the reduction in $G(H_2)$ by addition of N_2O is taken to be the yield of hydrogen from ion–neutralization. The two estimates are not necessarily directly comparable because the former refers to hydrogen atoms while the latter refers to H_2.

2.1.2. Free Radical Processes

Many important details of the mechanism by which H, NH_2 and NH lead to observed products are uncertain because of the lack of good specific rate data for many of the possible elementary processes.

Evidence from radiolysis of NH_3 in the presence of radical–scavengers indicates that most of the observed yield of H_2 results from processes involving free radicals. Non–radical processes yield only about 0.8 molecule of H_2 per 100 eV (table 2.2.1). At temperatures near 20°C radical sources of H_2 include reactions (13′), (22), (24) and possibly (28) followed by (29). At higher temperatures (23) is also important (see sec. 3.2.3).

TABLE 2.2.1. *Yields of intermediates in radiolysis of gaseous ammonia*

Species	Yield[a](g)	Radiation	Method of Determination	Comments	Reference
H	5.1–12.5	—	—	Preferred value is 10.4. See table 2.2.2 and section 2.2.1.	—
NH_2	10.4	1.0–1.7 MeV e⁻	Anal. of yields from NH_3	Calculated on the basis of an assumed mechanism. Pulse radiolysis, very high dose rate (10^{27} eV·g⁻¹s⁻¹).	Boyd..71–0216
NH_2	8.4	2 MeV e⁻	$g(NH_2) = g(NH_4^+)/$(fraction of NH_2 from NH_4^+)	Assume $g(NH_4^+) = 100/W$; estimate fraction of NH_2 from NH_4^+ by studies of $NH_3 - SF_6$. Pulse radiolysis.	Gordon..71–0169
NH_2	14	1 MeV e⁻	Assume $g(NH_2) = 2g(H_2) + g(H)$	Value probably too high. Based on the unlikely assumption that reaction (12) is exclusive source of non–radical H_2 (see section 2.2.2.) and $g(H) = 12.5$ (from $NH_3 - N_2H_4$).	Jones.67–0270
NH_2	11.9 – 2·g(NH)	⁶⁰Co–γ	Based on material balance: $g(NH_2) + 2g(NH) = g(H) + 2g(H_2)$.	$g(H) = 10.4^b$; $g(H_2) = 0.75$. Assuming $g(NH) = g(H_2)$, preferred value is $g(NH_2) = 10.4$.	Eyre.70–0479
NH	0.74	1.0 – 1.7 MeV e⁻	Anal. of yields from NH_3	See comments for NH_2. Preferred value is $g(NH) = 0.75$	Boyd..71–0216
NH	0.4	250 keV e⁻	UV spectroscopy	Pulse radiolysis. Yield is low. Used N_2O as dosimeter and assumed $G(N_2) = 9.68$. Accepted value at dose rate $< 10^{19}$ eV·g⁻¹s⁻¹ is $G(N_2) = 10.0$ (66–0434); $G(N_2)$ is 12.4 at 10^{27} eV·g⁻¹s⁻¹ (68–0318). Dose rate employed here was ~ 10^{26} eV·g⁻¹s⁻¹.	Meaburn.68–0101
H_2	0.7 – 0.8	—	—	See table 2.2.3. Preferred value is 0.75.	—
NH_4^+	3.9	⁶⁰Co–γ	Decrease in $G(H_2)$ when SF_6 (0.2%) is added to $NH_3 + C_3H_8$ (1.5%).	Agrees well with value calculated from $W = 26.5$ eV per ion pair for e⁻–radiation (64–0177) if essentially all positive ions converted to NH_4^+ before neutralization.	Johnson.68–0659, 67–0369
NH_4^+	3.5	⁶⁰Co–γ	Decrease in $G(H_2)$ when SF_6 is added to $NH_3 -$ isopropanol (0.5%).	—	Eyre.70–0479
NH_4^+	3.3	⁶⁰Co–γ	Decrease in $G(H_2)$ when N_2O is added to $NH_3 -$ isopropanol (0.5%)	—	Eyre.70–0479
NH_4^+	4.0	⁶⁰Co–γ	Decrease in $G(H_2)$ when CCl_4 is added to $NH_3 -$ isopropanol (0.5%).	—	Eyre.70–0479

a. Unless otherwise indicated yields were measured at ~ 20°C and ~ 1 atm. Yields are in ions, radicals or molecules per 100 eV and refer to the total yield of the intermediate from reaction 1 and from primary and secondary reactions of the ions and excited states produced in reactions 1 and 2 (table 2.1).

b. Eyre and Smithies (70–0479) distinguish between H atoms produced by ion neutralization and those produced by other reactions (such as 3 and 5). No such distinction is made in this paper and the value 10.4 refers to the total yield of H atoms (calculated from $g(H)$ and $g(e^-)$ values reported by Eyre and Smithies).

TABLE 2.2.3. *Primary yield of H_2*[a]

Yield(g)	Radiation	Method	Comments	Reference
0.81	$^{60}Co-\gamma$	Limiting value of $G(H_2)$ in presence of propylene.	Assume[b] $H + C_3H_6 \rightarrow C_3H_7$, $NH_2 + C_3H_6 \rightarrow C_3H_6NH_2$. $G(N_2)$ reduced from 1.45 to ~ 0.3.	Eyre.70-0479
0.80	$^{60}Co-\gamma$	As above.	$G(N_2)$ reduced from 1.9 to $\leqslant$0.3.	Johnson.68-0659
0.70 – 0.82	$^{60}Co-\gamma$	As above.	——	Nishikawa..67-0263
0.84	250 keV e^-	As above.	Pulse radiolysis.	Meaburn.68-0101
1.4	Fast e^-	As above.	High value may be result of failure to correct for H_2 from C_3H_6.	Sorokin.65-0523
0.74	1.0 – 1.7 MeV e^-	Kinetic analysis of product yields from pure NH_3.	Pulse radiolysis. Very high dose rate ($\leqslant 10^{26}eV \cdot g^{-1}s^{-1}$)	Boyd..71-0216
0.75	1 MeV e^-	Limiting value of $G(H_2)$ in presence of ethylene.	Acts similarly to propylene. $G(N_2)$ reduced from 1.5 to $\geqslant$ 0.6.[c]	Jones67-0270
0.74	$^{60}Co-\gamma$	As immediately above.	Also used C_2D_4.	Nishikawa.68-0051, 67-0263
0.84	$^{60}Co-\gamma$	Limiting value of $G(H_2)$ in presence of benzene.	Assume[d] $H + C_6H_6 \rightarrow C_6H_7$. $G(N_2)$ reduced from 1.45 to ~ 0.3.	Eyre.70-0479
1.0	$^{60}Co-\gamma$	As immediately above.	$G(N_2)$ reduced from 1.4 to 1.0. Aniline not detected.	Carstensen67-0701
0.8	$^{60}Co-\gamma$	As immediately above.	——	Johnson.68-0659

a. Unless otherwise indicated yields were measured at ~ 20°C and ~ one atmosphere. Yields are in molecules per 100 eV and refer to total yield of H_2 from reaction 1 and from primary and secondary reactions of the ions and excited states produced by reactions 1 and 2 (table 2.1).

b. Charge exchange between NH_3^+ and C_3H_6 is energetically possible but should be negligible at concentrations involved. Proton transfer from NH_4^+ to C_3H_6 ruled out on basis of proton affinities: ~ 9.2 and 6.6 eV for NH_3 and C_3H_6, respectively (62-9017).

c. N_2 determined mass spectrometrically. Presence of C_2H_4 led to analytical difficulties.

d. Charge exchange between NH_3^+ and C_6H_6 is energetically possible but should be negligible at concentrations involved. Proton transfer from NH_4^+ is probably ruled out on basis of proton affinities: ~ 9.2 and $\leqslant$ 6.3 eV (62-9017).

made for energy absorbed in the additive. Results with a variety of additives are in good agreement and lead to $g(H_2)$ = 0.75. .

Relatively few values of $g(NH_2)$ have been reported. Gordon, Mulac, and Nangia (71-0169) estimate $g(NH_2)$ = 8.4 from $g(NH_4^+)$ and the fraction of NH_2 produced by neutralization of NH_4^+. They assume $g(NH_4^+)$ = 100/W (W is the energy in eV to produce an ion pair) and estimate the fraction of NH_2 produced by neutralization of NH_4^+ from a comparison of results of irradiation of pure NH_3 and of NH_3 in the presence of SF_6. Jones and Sworski (67-0270) have suggested $g(NH_2)$ = $g(H)$ +2$g(H_2)$ on the basis of the unlikely assumption that non-radical H_2 arises exclusively via reaction (12). As noted earlier (sec. 2.1.1) studies of mixtures of NH_3 and CCl_4 indicate $g(12)$ ~ 0.1 (68-0051) whereas $g(H_2)$ = 0.75. Reaction (4) probably accounts for a significant fraction of non-scavengable H_2. In photochemistry 12 – 14% of the dissociation at 147 and 123.6 nm (64-7003, 62-0132) is attributed to (4),

$$(4) \quad NH_3* \rightarrow NH + H_2$$
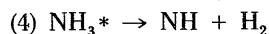
and NH has been observed spectroscopically by Meaburn and Gordon (68-0101) in pulse radiolysis of NH_3. Meaburn and Gordon estimate $g(NH)$ ~ 0.4, but this is probably low because of an error in dosimetry (table 2.2.1). On the basis of material balance one expects $g(NH_2)$ =$g(H)$ + 2$g(H_2)$ – 2$g(NH)$. The best assumption seems to be that $g(NH)$ $\cong$ $g(H_2)$ and this leads to a preferred value of 10.4 for $g(NH_2)$.

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approximately 20°C and one atmosphere pressure are summarized in section 3.1, and the influence of various parameters is discussed in 3.2.

3.1. Product Yields for Radiolysis Under
Static Conditions at ~ 20°C and ~ 1 Atmosphere

H_2 and N_2 are the only measurable products at dose rates up to at least $2 \times 10^{18} eV \cdot g^{-1} s^{-1}$ (table 3.1.1); $G(H_2) = 5.0 \pm 1.0$ and $G(N_2) = 1.7 \pm 0.3$. Presumably, the steady—state concentration of hydrazine is kept very low because of radical—hydrazine reactions (see sec. 2.1.2).

At very high dose rates ($\geqslant 10^{26} eV \cdot g^{-1} s^{-1}$) hydrazine is produced in significant yield in static systems (71—0216, 69—0272) because radical—product reactions do not compete effectively with radical—radical reactions. Hydrazine is also a product in flow systems (see sec. 3.2.6).

In all cases the total dose was sufficiently low to preclude variations in product yields associated with high conversion (see sec. 3.2.1). Indeed, the only obvious variables are dose rate and the LET (linear energy transfer), of the radiation. Both of these factors may contribute to the relatively large scatter in yields but it is clear from table 3.1.2 that they alone are not responsible. Other probable contributing factors include the presence of trace impurities and problems in dosimetry. The neutralization process in particular should be quite sensitive to trace impurities, the presence of which would probably lead to low yields (see sec. 2.1.1). Most of the results summarized in this sec. are based on dosimetry with nitrous oxide. Problems associated with gas phase dosimetry in general (71—0062, 67—0546, 71—0179) and the nitrous oxide dosimeter in particluar (71—0062, 68—0318, 67—0027, 66—0434, 61—0103) have been discussed elsewhere.

TABLE 3.1.1. *Product yields from radiolysis of gaseous ammonia with various radiations under static conditions at ~ 20°C and ~ 1 atm*[a]

Radiation	$G(-NH_3)$	$G(H_2)$	$G(N_2)$	$G(N_2H_4)$	Dose Rate $(eV \cdot g^{-1} s^{-1})$	Comments	Reference
1 MeV e⁻	3.0	4.5	1.5	0.0	2×10^{18} [b]	Yields depend upon dose rate. See section 3.2.2	Jones.67—0270
1.0 – 1.7 MeV e⁻	——	3.6	1.0	0.58[c]	2×10^{26} and 2×10^{27} [d]	Pulse radiolysis.	Boyd..71—0216 and Willis..69—0272
~ 250 keV e⁻	——	2.3[e]	0.68[e]	0.07[e]	~ 10^{26} (4.0 $\times 10^{18}$ eV/pulse).[e]	Pulse radiolysis.	Meaburn.68—0101
⁶⁰Co—γ	2.7 – 4.7	4.1 – 7.0	1.4 – 2.3	0.0 – 0.001	——	See table 3.1.2.	——
¹H⁺ (0.8 MeV)	4.0	6.0	2.0	0.0	≅ 3×10^{15} [f]	Yields depend on dose rate. See section 3.2.2	Horscroft64—0174
²H⁺ (2 MeV)	——	——	——	0.5	not reported	No attempt to measure $G(H_2)$ or $G(N_2)$.	Lampe...63—0098
⁴He²⁺	3.0 – 4.2[g]	——	——	——	——	See table 3.1.3.	——
Reactor (γ + n)	3.8	5.7	1.9	—	—	——	Dolle58—0051

a. For yields at other temperatures and pressures see section 3.2.

b. N_2O dosimetry; $G(N_2) = 10.0$ (66—0434).

c. N_2H_4 is a significant product in static system only when dose rate is high enough to reduce the importance of radical—N_2H_4 reactions.

d. N_2O dosimetry; $G(N_2) = 12.4$. Value obtained by adiabatic calorimetry (68—0318). Probably applies only to very high dose rates.

e. These values are probably low because they are based upon N_2O dosimetry with $G(N_2) = 9.68$. Generally accepted value is $G(N_2) = 10$ for dose rates less than about $10^{19} eV \cdot g^{-1} s^{-1}$. Value may be higher at higher dose rates (see d above). The dose rate is estimated from the dose per pulse on the basis of a cell volume of 0.68 liters and a pulse duration of ~ 40 ns.

f. Dosimetry based on charge collection; value in $eV \cdot g^{-1} s^{-1}$ involves estimate of effective volume. This is lowest dose rate employed.

g. Most yields originally reported as molecules per ion pair (M/N); these have been converted to G assuming $W = 30.5$ eV per ion pair in NH_3 for ⁴He²⁺ radiation (53—0008).

3.2. Effect of Various Parameters

3.2.1. Dose

At dose rates such that H_2 and N_2 are the only products, $G(H_2)$ and $G(N_2)$ are independent of total dose up to at least 8×10^{22} eV/g (table 3.2.1). At very high conversions, yields should decrease because of $NH_2 + H_2 \rightarrow NH_3 + H$ (64–0174, 32–0002). The inhibiting effect of H_2 has been observed in photochemical studies of NH_3 (55–7001, 44–7000).

At dose rates of the order of 10^{26} eV·$g^{-1}s^{-1}$, N_2H_4 is a product and because N_2H_4 reacts with H and NH_2, product yields may be independent of dose over a more limited range. Available data indicate independence of dose extends at least up to 6×10^{20} eV/g (at 10^{27} eV·$g^{-1}s^{-1}$) (69–0272). At these high dose rates the total dose is delivered as a series of pulses of very short duration (50–100 ns).

TABLE 3.2.1. *Effect of dose*

Radiation	Effect of $G(-NH_3)$[a]	Max. Dose (eV/g)	Reference
Fast e⁻	none	8×10^{22} [b]	Sorokin.65–0523
Fast e⁻ (1 MeV)	none	4.5×10^{21}	Jones.67–0270[c]
^{60}Co–γ	none	3×10^{22}	Kazanjian.68–0555[d]
^{4}He^{2+}(^{210}Po)	none	6×10^{22}	Kazanjian.68–0555
^{1}H$^+$(0.8 MeV)	none	6×10^{21} eV totally absorbed in 0.5 cm³.	Horscroft64–0174

a. At dose rates employed N_2 and H_2 were the only products observed. Relevant dose rates can be found in tables 3.1.1 and 3.1.2.
b. Corresponds to about 5% conversion.
c. See also 69–0272 for results with fast e⁻ at very high dose rate (10^{27} eV·$g^{-1}s^{-1}$).
d. See also 58–0051, 64–1757, 67–0701, 70–0134.

3.2.2. Dose Rate

At pressures near one atmosphere $G(-NH_3)$ decreases with increasing dose rate (table 3.2.2) and the magnitude of the effect decreases with decreasing pressure (67–0271, 34–0003).

Sorokin and Pshezhetskii (65–0523) report $G(-NH_3)$ independent of intensity; however, their investigation was limited to a relatively small (eight–fold) variation in dose rate. The results of Jones, Sworski and Williams (67–0271) obtained under similar conditions, but for a much wider (100–fold) variation in dose rate, indicate that $G(-NH_3)$ should change only by about 10% over the range employed by Sorokin and Pshezhetskii.

Burtt and Baurer (55–0010) and Burtt and Zahlen (57–0018) have reported $G(-NH_3)$ increases with increasing intensity at 200 torr but the intensities were much lower than are usually encountered (table 3.2.2).

The observed decrease in $G(-NH_3)$ with increasing dose rate has not been satisfactorily explained. No effect is expected on the basis of the simple mechanism discussed in sections 2.1.1 and 2.1.2. That mechanism assumes that ions and excited neutrals produced in the early stages of radiolyisis undergo reactions that lead principally to NH_2, H, NH, and H_2. The radicals in turn react with each other and with other intermediates such as N_2H_4 and N_2H_3 to give the observed products.

If reaction (23) is included in the mechanism, $G(-NH_3)$ would

$$(23)\ H + NH_3 \rightarrow H_2 + NH_2$$
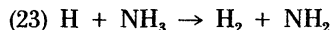
be expected to decrease with increasing intensity. The specific rate of (23) has not been accurately measured but estimates of 5 dm³mol^{-1}s^{-1} (65–0555) and 200 dm³mol^{-1}s^{-1} (69–0272) have been reported for temperatures near 20°C. If k_{23} is in fact as high as 200 dm³mol^{-1}s^{-1}, reaction (23)

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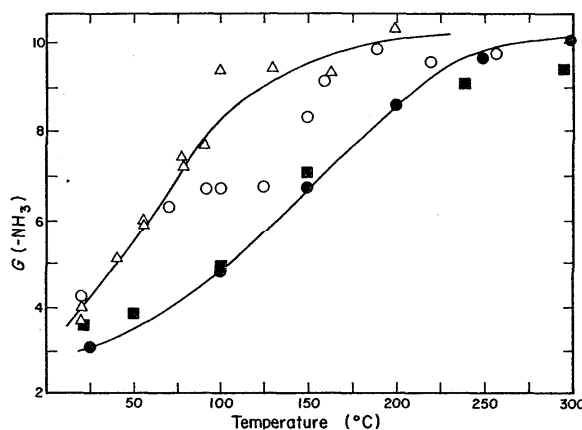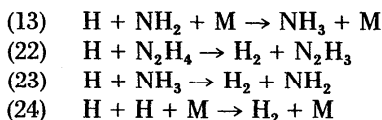FIGURE 3.2.3.1. *Variations of $G(-NH_3)$ with temperature at dose rates less than $10^{19}eVg^{-1}s^{-1}$.* Original data in terms of $G(H_2)$; $G(-NH_3)=2/3\ GH_2$). ○ 67–0546 (7.0 x $10^{15}eV\cdot g^{-1}s^{-1}$); ● 67–0270 (2.0 x $10^{18}eV\cdot g^{-1}s^{-1}$); △ 68–0659 (1.4 x $10^{16}eV\cdot g^{-1}s^{-1}$); ■ 70–0479 (3 x $10^{15}eV\cdot g^{-1}s^{-1}$).

Solvation of NH_4^+ in gaseous ammonia is known to occur (68–0032, 66–9067, 64–9015) and modification of ion–neutralization in the manner suggested is not unreasonable. However, considerably higher temperatures than these are required to produce the necessary changes in solvation (68–0032, 66–9067). For example at 100°C and 1 torr n = 2 and neutralization to give more than one H is still endothermic (69–0326, 66–9067). Also, Johnson and Simic (68–0659) have found $G(H_2)$ from mixtures of ammonia and propane and depression of $G(H_2)$ from such mixtures by SF_6 are independent of temperature, and they conclude that the hydrogen yield from neutralization of NH_4^+ by e^- is independent of temperature.

Jones and Sworski (67–0270) have interpreted the effect of temperature in terms of competition between reactions (13), (22), (23) and (24).

(13) $H + NH_2 + M \rightarrow NH_3 + M$
(22) $H + N_2H_4 \rightarrow H_2 + N_2H_3$
(23) $H + NH_3 \rightarrow H_2 + NH_2$
(24) $H + H + M \rightarrow H_2 + M$

They assume that reaction (23), which has an energy of activation of 10–15 kcal/mol (62–0131) is unimportant at room temperature but becomes significant at higher temperatures. Johnson and Simic (68–0659) reject this interpretation on the basis that the energy of activation for reaction (23) is too high to account for their observed temperature dependence. They suggest that increase in $G(-NH_3)$ with temperature is best explained in terms of competition between reactions (13) and (22). An Arrhenius plot of their data leads to an apparent energy of activation of about 2.1 kcal/mol. (A similar treatment of the data of Jones and Sworski (67–0270) leads to a value of 1.7.) In terms of their mechanism this apparent energy of activation is to be identified with the differences in activation energies of reactions (22) and (13). Reaction (22) has been reported to have an activation energy of 2.0 kcal/mol (62–0131) while (13) would be expected to have an activation energy near zero. Thus, the observed temperature dependence agrees well with their mechanism. An important implication of this mechanism is that reaction (23) is unimportant at least up to 200°C. However available specific rate data indicates that reaction (23) should compete favorably with reaction (22) at temperatures at least as low as 150°C. For example if the reasonable assumption is made that the concentration of NH_3 is at least 10^3 times greater than the steady state concentration of N_2H_4, reaction (23) is about four times faster than reaction (22) at 150°C (specific rates from 62–0131; see also table 2.1).

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TABLE 3.2.4. *Effect of pressures*[a]

Radiation	Pressure Range	Effect on $G(-NH_3)$	Reference
1 MeV e^-	$47 \rightarrow 800$ torr	See fig. 3.2.4 for results at 23°C; At 200°C, $G(-NH_3)$ is independent of P.	Jones..67–0271
Fast e^- [b]	$50 \rightarrow 500$ torr (20°C)	Decreases with increasing P; appears to approach limit at ~ 500 torr. G not given.	Sorokin.65–0523
^{60}Co–γ	$200 \rightarrow 650$ torr (23°C)	See fig. 3.2.4.	Carstensen67–0701
^{60}Co–γ	$100 \rightarrow 760$ torr (23°C)	None.	Buchanan.70–0134
^{60}Co–γ	400 torr $\rightarrow 3.2$ atm (41°C)	None.	Johnson.68–0659
^{60}Co–γ	$100 \rightarrow 700$ torr (20°C)	None.	Eyre.70–0479
^{1}H$^+$	$200 \rightarrow 600$ torr (22°C)	Decrease linearly with increasing P, from 1.93 to 1.73.	Horscroft64–0174
^{4}He^{2+}	$80 \rightarrow 700$ torr (20°C)	Decrease with increasing P; total decrease of 23%.[c]	Luyckx34–0003[d]
^{60}Co–γ	$1 \rightarrow 12$ atm (20°C)	None.	Nishikawa.68–0051
^{60}Co–γ	$1 \rightarrow 60$ atm (120°C)	P(atm), $G(-NH_3)$; 1, 10; 7.7, 15; 9, 14.8; 30, 9.0; 60, 6.6.	Sorokin.64–1757
^{60}Co–γ	1 atm $\rightarrow 0.312$ g/cm^3(137°C)	Sharp decrease from 4.1 to 1.4 at density near 0.15 g/cm^3.	Toi..62–0074[e]

a. In all cases incident intensity was constant and therefore variation in pressure is accompanied by a variation in energy absorbed per unit volume per unit time.
b. Energy not specified.
c. Author attributes important but unspecified part of this decrease to changes in absorbed intensity. See a above.
d. See also 57–0018.
e. See also 69–0026.

$G(-NH_3)$ increases from about 2.9 to a maximun of about 4 at 100 torr. Buchanan and Hanrahan (70–0134) failed to observe a similar increase in their study of ^{60}Co–γ radiolysis of NH$_3$. They found $G(-NH_3)$ independent of pressure from one atmosphere to 100 torr, the lowest pressure studied. Eyre and Smithies (70–0479) also found $G(-NH_3)$ independent of pressure over this same pressure range.

Luyckx (34–0003) observed an increase in $G(-NH_3)$ of about 23% for a decrease in pressure from 700 to 80 torr in a study of ^{4}He^{2+} radiolysis of ammonia. He attributed an important, albeit unspecified, part of this decrease to the accompanying variations in intensity. Under conditions of constant incident intensity a decrease in pressure is accompanied by a decrease in the energy absorbed per unit volume per unit time. All of the studies summarized in table 3.2.4 were carried out under such conditions; however, the decrease in intensity associated with a change in pressure from one atmosphere to about 100 torr should not affect $G(-NH_3)$ by more than about 10% (see sec. 3.2.2).

Burtt and Zahlan (57–0018) tried to determine the effect of pressure in the range 700 – 70 torr under conditions of nearly constant intensity using ^{4}He^{2+} radiation. They conclude that $G(-NH_3)$ increases with decreasing pressure but the experimental data are limited and not especially convincing.

Horscroft (64–0174) has reported an essentially linear increase in $G(-NH_3)$ of about 10% between 600 and 200 torr in radiolysis with 0.8 MeV protons. At the dose rate employed, intensity effects should be very small (section 3.2.2.) and the 10% increase in $G(-NH_3)$ can probably be attributed solely to the decrease in pressure.

Luyckx (34–0003) has pointed out that his results suggest the existence of an "inversion intensity." Near this "inversion intensity", $G(-NH_3)$ is relatively insensitive to changes in pressure. At higher intensities $G(-NH_3)$ decreases with increasing pressure and at lower intensities it increases with increasing pressure. The inversion intensity arises because $G(-NH_3)$ is independent of intensity at pressures below about 140 torr but decreases with increasing intensity at higher pressures. This may account for some of the discrepancies that have been observed.

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3.2.5. Electric Field

Electric fields have been applied to systems during radiolysis to obtain information about the role of ion—neutralization processes (for a general discussion of this technique see G.G. Meisels, 68–0650, page 364). In the case of ammonia, electric fields less than about 5 $V \cdot cm^{-1}$ $torr^{-1}$ do not significantly affect $G(-NH_3)$.

The earliest investigations (38–0002, 42–0001, 55–0010, 57–0018) were carried out with relatively low—intensity ($10^{13} - 10^{14}$ $eV \cdot g^{-1} s^{-1}$) $^4He^{2+}$ radiation over a pressure range of 200 to 620 torr at 25°C. In the first of these (38–0002), a significant decrease ($\sim$ 30%) in $G(-NH_3)$ with increasing field strength was reported at 620 torr, and on the basis of this observed decrease it was concluded that 34% of the overall reaction was attributable to ion—recombination. However, this decrease was not observed in subsequent studies under similar conditions in the same laboratory using more highly purified ammonia (55–0010, 57–0018).

More recently, Jones and Sworski (67–0270) carried out a study of the effect of applied field upon radiolysis with 1 MeV electrons. At 200 torr and 23°C they find $G(-NH_3)$ is independent of field strength up to about 5 $V \cdot cm^{-1}$ $torr^{-1}$; $G(-NH_3)$ increases with increasing field strength above 5 $V \cdot cm^{-1}$ $torr^{-1}$ because of excitation of NH_3 by collision with electrons accelerated in the field. These results suggest that the net chemical effect of ion—neutralization is the same whether the neutralization occurs homogeneously or at a surface.

3.2.6. Flow Rate

Most studies of gaseous ammonia have been made under static conditions. In such cases, hydrazine is not obtained in measurable yields at dose rates below $\sim 10^{26} eV \cdot g^{-1} s^{-1}$ (69–0272, 68–0101) presumably because of radical—hydrazine reactions. Jones, Sworski and Williams (67–0271) have studied radiolysis of NH_3 in this low dose rate range with 1 MeV electrons under both static and flow conditions. Hydrazine is not produced in measurable yields under static conditions but it is an important product in flow systems. Yields of N_2H_4 increase with increasing flow rate and decreasing intensity. At constant flow rate and intensity, $G(N_2H_4)$ increases markedly with increasing temperature. At a constant beam current of 5 μA and constant flow rate of 2.5 dm^3/min, $G(N_2H_4)$ increases from 0.62 to 2.97 as the temperature is increased from 25°C to 300°C. The highest yield observed was $G(N_2H_4)$ = 3.95 for a beam current of 0.05 μA and a flow rate of 2.5 dm^3/min at 300°C.

In flow systems hydrazine is removed from the reaction zone and rapidly diluted so that radical—hydrazine reactions are considerably less important than in static systems. Increasing temperature and decreasing intensity further reduce the probability of such N_2H_4—consuming reactions. An increase in temperature is assumed to increase the importance of reaction (23) relative to the reaction of H with N_2H_4, and decrease

$$(23) \quad H + NH_3 \rightarrow H_2 + NH_2$$
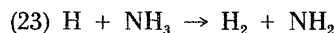
in intensity probably favors production of N_2H_4 by reducing the steady—state concentration of H.

TABLE A.1.2. *Properties of ionic species*[a]

Ion	ΔH_f° (298.2 K) (kcal/mol)	$A.P.$ (eV)	Relative abundance $(2 \times 10^{-7} \text{ torr})$	Comments
NH_4^+	154 (55–9002)	—	0	Accounts for 97% of positive ions at 1 torr (66–0298) because of rapid ion–molecule reactions. Solvated at normal temperatures and pressures (66–9067, 68–0032, 64–9015, 65–0775, 71–9024).
NH_3^+	223	10.2	100	Rapidly converted to NH_4^+ at P near 1 torr (66–0298).
NH_2^+	304	16.0	40.92	Rapidly converted to NH_4^+ at P near 1 torr (66–0298).
NH^+	382	17.1 (+H_2) 21.6 (+2H)	4.50	See table 2.1 for reactions of NH^+.

a. Unless otherwise indicated values have been taken from the following sources. Standard heats of formation (ΔH_f°) and appearance potentials ($A.P.$), Wagman.....68–9060; relative abundances, Melton 66–0298.

TABLE A.2.1. *Additives: Binary mixtures* – Continued

Additive	Concn. range, mol %	Radiation	Comments	Reference
Nitric Oxide	$0 \to 13$	^{60}Co–γ	Reduced $G(H_2)$ to 0.69. $G(N_2)$ = 11.9 and presumably $G(N_2)$ = $g(NH) + g(NH_2)$.	Eyre.70–0479
	$0 \to 0.7$	2 MeV e⁻	Pulse radiolysis. Studied effect of NO on decay of NH_2 and NH. Calculate specific rates for NO + NH and NO + NH_2.	Gordon..71–0169
Oxygen	$0 \to 3 \times 10^{-3}$	^{60}Co–γ	$G(H_2)$ and $G(N_2)$ reduced.	Carstensen67–0701
Oxygen	$0 \to 6$	250 keV e⁻	Pulse radiolysis, no yield data. Report reduction in $t_{0.5}$ for decay of NH in presence of O_2.	Meaburn.68–0101
Phosphine	$0 \to 100$	^{60}Co–γ	Yields consistent with $NH_2 + PH_3 \to NH_3 + PH_2$ $H + PH_3 \to H_2 + PH_2$ $2PH_2 \to PH_3 + PH$ $2PH \to P_2 + H_2$.	Buchanan.70–0653
Propane	$0 \to 6.6$	^{60}Co–γ	Used to estimate $g(H)$. See section 2.2.1 and also table A.2.2.	Johnson.68–0659
Propane	$0 \to 8.6$	^{60}Co–γ	ditto.	Nishikawa..69–0326[c]
Propane	$0 \to 20$	^{60}Co–γ	ditto. Find $G(H_2)$ depends upon dose.	Eyre.70–0479
Propylene	1.5	^{60}Co–γ	Used to determine $g(H_2)$. See table 2.2.3.	Johnson.68–0659
Propylene	$0 \to 3.8$	^{60}Co–γ	ditto.	Nishikawa..67–0263
Propylene	$0 \to 5$	^{60}Co–γ	ditto.	Sorokin.64–1757
Propylene	$0 \to 7.4$	^{60}Co–γ	ditto.	Eyre.70–0479
Propylene	$0 \to 9$	fast e⁻ [a]	ditto.	Sorokin.65–0523
Propylene	$0 \to 8$	1.0 – 1.7 MeV e⁻	Pulse radiolysis. Very high intensity.	Willis..69–0272
Propylene	$0 \to 3.3$	250 keV e⁻	Pulse radiolysis. Results in increases in $G(N_2H_4)$ (0.07 to 0.18).	Meaburn.68–0101
Propylene	$0 \to 10$	2 MeV e⁻	Pulse radiolysis. Studied effect of C_3H_6 on decay of NH_2.	Gordon..71–0169
Sulfur hexafluoride	$0 \to 1.1$	^{60}Co–γ	Very limited study. See also table A.2.2.	Nishikawa.69–0326
	$0 \to 10$	2 MeV e⁻	Pulse radiolysis. Studied effect of SF_6 on decay of NH_2. Used to estimate importance of ion–neutralization.	Gordon..71–0169
Xenon	$0 \to 56$	0.8 MeV ^{1}H⁺	Efficient energy transfer from Xe to NH_3.	Horscroft64–0174
Xenon	$0 \to 80$	^{60}Co–γ	ditto.	Sorokin.65–0523
Xenon	~ 24	X–rays (40 kV)	ditto.	Guenther.37–0001

a. Energy not specified.
b. See also 67–0263.
c. See also 68–0505 and 69–0326.

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