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October 1972

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Radiation Research

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RADIATION CHEMISTRY OF GLYCYLGLYCINE

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Abstract

A study has been made of the radiation chemistry of glycylglycine in oxygen-free systems. These include dilute and concentrated solutions as well as the solid state. Detailed reaction stoichiometries for each system are formulated on the basis of product analysis. Specific contributions of radicals ions and excited molecules in the formation of products are discussed.

Radiolysis

Peptides

Oxygen-free systems

RADIATION CHEMISTRY OF GLYCYLGLYCINE IN OXYGEN-FREE SYSTEMS[1]

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Radiation-induced reactions of the α-amino acids in the uncombined form have been studied quite extensively both in aqueous solution and in the solid state (1). Similar attention has been given to the radiation chemistry of certain peptide forms of these amino acids such as the N-acyl and polyamino acid derivatives (1,2). However, no systematic and detailed radiation-chemical study of the peptide series

$$NH_2CHRCO(NHCHRCO)_\eta NHCHRCOOH$$
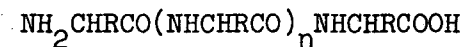
has been made over a range of molecular weight.

We have undertaken such a study and in the present paper we examine the radiation chemistry of the simplest member of this series viz. glycylglycine ($\eta=0$). Work described here is confined to oxygen-free systems. The radiation chemistry of glycylglycine in oxygenated solution has been described in an earlier paper (3).

EXPERIMENTAL

The glycylglycine was obtained from Nutritional Biochemicals and was recrystallized from distilled water to remove trace amounts of ammonia. Water used in preparation of solutions was from a Barnstead still and was redistilled first from alkaline permanganate and then from phosphoric acid.

Both liquid and solid samples were de-gassed on the vacuum line, sealed off, and irradiated with ^{60}Co γ-rays at a dose rate of 7×10^{17} ev/gm-min. Dosage was determined with the Fricke dosimeter [$G(Fe^{3+} = 15.5$, $\epsilon_{305} = 2180$ at $24°C$]. All yields are expressed as G values (molecules per 100 ev absorbed energy). Energy deposition in solids and solutions was taken to be proportional to electron density. The irradiated solid samples were dissolved to a concentration of ~ 1 $\underline{M}$ in redistilled water under nitrogen in preparation for subsequent analysis.

Free ammonia and amide ammonia were determined by use of a modification of the micro-diffusion method of Conway (4). Diffusates were assayed with Nessler reagent. In the determination of free ammonia, the sample solutions were diluted three-fold with saturated K_2CO_3 solution in the outer chamber of the diffusion cell; recovery of ammonia in the acid compartment ($0.1N$ H_2SO_4) is complete in three hours. For total ammonia (free plus amide), a second sample was placed in a diffusion cell and made 2N in NaOH; under these conditions the amide hydrolysis and ammonia transfer is complete in 24 hours.

A series of control runs established that the above procedures are adequate for the separate determination of free ammonia and amide ammonia when the latter represents the minor component as is the case in the present system.

However, at the higher (amide)/(ammonia) ratios observed in other systems (3),

hydrolysis of the amide in the Na_2CO_3 solution becomes appreciable and other

modifications of the method must be employed.

Free acetic acid was separated through lyophilization of the sample

solution after acidification with H_2SO_4. The volatile fraction was neutralized

and concentrated to a minimal volume. This was then re-acidified and the acetic

acid component was identified and assayed by vapor-phase chromatography after

the method of Baker (5).

Acetylglycine was separated by passing the sample solution through

Dowex 50 in the acid form. Glycylglycine and all products containing the free

amino group are quantitatively removed. Acetylglycine and free acetic acid

pass through the column with little or no fractionation or retention. The

effluent was collected and lyophilized to remove water and any free acetic

acid. The N-acetylglycine in the residue was identified and qualitatively

estimated through application of the techniques of filter-paper chromatography (6).

The quantitative determination of N-acetylglycine was based on measurements of

free acetic acid released on hydrolysis of the product in dilute H_2SO_4. The

acetic acid assay techniques used were identical to those employed in the

determination of free acetic acid as an initial product (see above).

All other products were determined after hydrolysis in 2N HCl at 95°C

for 24 hours.

The carbonyl products (glyoxylic acid and formaldehyde) in the hydro-

lyzate were identified through filter-paper chromatography (7). The quantita-

tive determinations of glyoxylic acid and formaldehyde were made after the

methods of Friedmann and Haugen (8) and of Johnson and Scholes (9) respectively, with the modifications introduced by Sokol.[2]

In the determinations of glycolic acid, succinic acid, aspartic acid, and diaminosuccinic acid the hydrolyzate was lyophilized to dryness prior to assay.

In the measurement of glycolic acid the residue was redissolved in a minimum volume of water and assayed colorimetrically, using the techniques and precautions outlined by Calkins (10). Succinic acid was extracted from the solid residue with acetone. The latter was evaporated off and the non-volatile fraction was treated with methanol containing $\sim$ 10 percent anhydrous hydrogen chloride. The methyl succinate so formed was identified and quantitatively determined by vapor-phase chromatography (5).

The aspartic acid and diaminosuccinic acid were isolated by ion-exchange chromatography after the method of Moore and Stein (11) as modified by Weeks and Garrison (12). In this procedure, the sample is placed on Dowex 50 (acid form) and then eluted with HCl in progressively increasing concentration (0 to 4N) to fractionally separate nitrogen products from parent glycine. The appropriate effluent fractions were collected and lyophilized to dryness. The samples were then treated with methanol containing $\sim$ 10 percent anhydrous hydrogen chloride to form the amino acid esters. These were in turn acetylated with trifluoroacetic anhydride. The volatile derivations were characterized and quantitatively determined by vapor-phase chromatography (13).

An extended series of control analyses of glycylglycine solutions containing the appropriate concentrations of the observed reaction products

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[2] H. A. Sokol, Lawrence Berkeley Laboratory, Report LBL-241.

established the quantitative applicability of the above methods to the present

system.   Determinations of all products listed in Table I with the exception

of the diaminosuccinic acid were reproducible to within ± 5 percent.   The

reproducibility of the diaminosuccinic acid yields from the aqueous systems

is in the order of ± 10 percent.   Yields of diaminosuccinic acid product from

the solid system could not be determined with any satisfactory reproducibility.

We have found no acceptable explanation for this peculiar finding; further

work is in progress.

RESULTS AND DISCUSSION

Dilute aqueous solution

In the γ-radiolysis of glycylglycine in dilute oxygen-free solution, we are concerned primarily with the chemistry initiated by reactions of the peptide with the oxidizing and reducing species formed in water radiolysis (14-16)

$$H_2O \xrightarrow{\hspace{1cm}} H_2O_2, H_2, OH, H, e_{aq}^-, H^+ \tag{1}$$
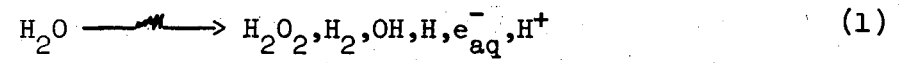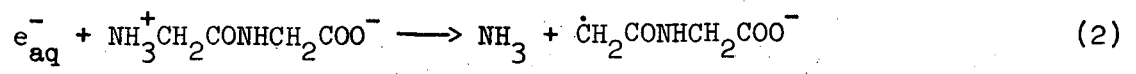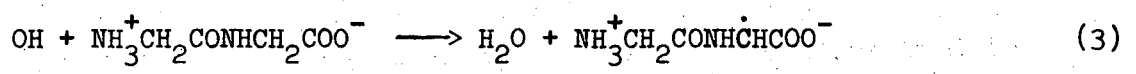
Studies (17,18) of the effects of added second-solutes on $G(NH_3)$ values from glycylglycine in oxygen-free solution indicated that the hydrated electron, e_{aq}^-, reacts essentially quantitatively with the glycylglycine zwitterion via

$$e_{aq}^- + NH_3^+CH_2CONHCH_2COO^- \longrightarrow NH_3 + \dot{C}H_2CONHCH_2COO^- \tag{2}$$

and that OH is removed via

$$OH + NH_3^+CH_2CONHCH_2COO^- \longrightarrow H_2O + NH_3^+CH_2CONH\dot{C}HCOO^- \tag{3}$$

The recent pulse-radiolysis studies of Simic and Hayon (19) and the ESR studies of Sevilla (20) are consistent with the assignments formulated in equations 2,3. The reductive deamination reaction 2 is analogous to that observed in earlier studies of the radiation chemistry of the free α-amino acids in oxygen-free solution (21,22).

We have now completed a detailed chemical study of final products formed in the γ-radiolysis of glycylglycine in oxygen-free solution and the results are summarized in columns 1,2 Table I. The experimental findings provide chemical support for reactions 2,3 as written and also provide information on the chemical properties of the organic radicals so formed.

The yield of free ammonia from .05$\underline{M}$ glycylglycine solution corresponds to $G(NH_3)_f \simeq 2.8 \simeq G_{e^-_{aq}}$. The total ammonia yield which includes "amide-like" ammonia plus free ammonia is appreciably greater i.e. $G(NH_3)_t \simeq 3.3$. This formation of amide-like ammonia is associated with the concomitant formation of the carbonyl products, glyoxylic acid and formaldehyde. The observed stoichiometry is interpreted as evidence that a fraction of the peptide radicals formed via OH attack in reaction 3 undergo subsequent oxidation via
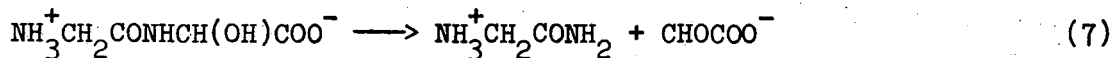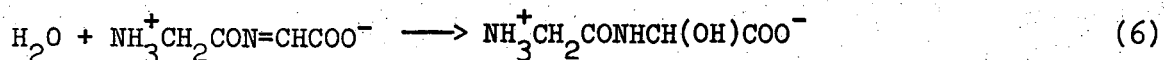
$$2NH_3^+CONH\dot{C}HCOO^- \longrightarrow NH_3^+CH_2CONHCH_2COO^- + NH_3^+CH_2CON=CHCOO^- \quad (4)$$

and

$$H_2O_2 + NH_3^+CH_2CONH\dot{C}HCOO^- \longrightarrow NH_3^+CH_2CONHCH(OH)COO^- + OH \quad (5)$$
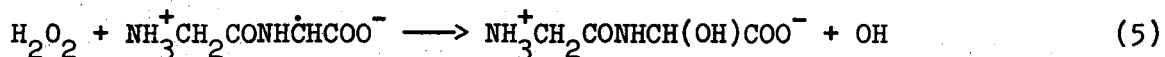
where the H_2O_2 of reaction 5 is derived from the radiation-induced step 1. The dehydropeptide derivatives formed in reactions 4,5 are labile and yield amide and carbonyl products

$$H_2O + NH_3^+CH_2CON=CHCOO^- \longrightarrow NH_3^+CH_2CONHCH(OH)COO^- \quad (6)$$

$$NH_3^+CH_2CONHCH(OH)COO^- \longrightarrow NH_3^+CH_2CONH_2 + CHOCOO^- \quad (7)$$

Consistent with this we find that carbonyl yield in .05M glycylglycine solution corresponds to $G \simeq 0.6$.

In the dilute glycylglycine solutions there appear to be two major paths for removal of the $\dot{C}H_2CONHCH_2COO^-$ radicals formed in the reductive deamination reaction 2. These are

$$NH_3^+CH_2CONHCH_2COO^- + \dot{C}H_2CONHCH_2COO^- \longrightarrow NH_3^+CH_2CONH\dot{C}HCOO^- + CH_3CONHCH_2COO^- \quad (8)$$

and

$$NH_3^+CH_2CONH\overset{\cdot}{C}HCOO^- + \overset{\cdot}{C}H_2CONHCH_2COO^- \longrightarrow NH_3^+CH_2CONHCHCOO^- \tag{9}$$
$$\underset{\underset{CH_2CONHCH_2COO^-}{|}}{}$$

In the .05M glycylglycine solution, reaction 8 produces acetylalanine with

G ≃ 0.9 and reaction 9 yields aspartic acid with G ≃ 1.1 as measured after

hydrolysis of the irradiated solution. The peptide radicals, $NH_3^+CH_2CONH\overset{\cdot}{C}HCOO^-$,

formed in reactions 3 and 8 are, as we have noted, consumed in part through

reactions 4,5 and 9; those remaining are ultimately removed through dimerization

$$2NH_3^+CH_2CONH\overset{\cdot}{C}HCOO^- \longrightarrow NH_3^+CH_2CONHCHCOO^- \tag{10}$$
$$\underset{\underset{NH_3^+CH_2CONHCHCOO^-}{|}}{}$$

The diaminosuccinic acid observed in the hydrolyzate with G ≃ 0.8 represents

the yield of reaction 10.

The chemistry of reactions 1-10 appears then to satisfactorily account

for the product stoichiometries observed in the γ-radiolysis of glycylglycine

in dilute oxygen-free solution.

Concentrated aqueous solution

On increasing the glycylglycine concentration from .05M to 1M, we find

that the yield of free ammonia increases from 2.8 to 3.8. This increase is

accompanied by a corresponding increase in the combined yields of acetylglycine

and aspartic acid which products are derived from the $\overset{\cdot}{C}H_2CONHCH_2COO^-$ radical.

The evidence is that the yield of the reductive deamination reaction 2 increases

with increasing glycylglycine concentration in qualitative accord with the
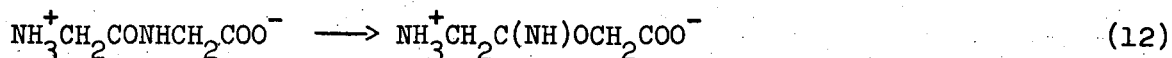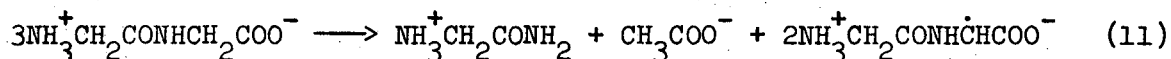
spur-diffusion model developed by Schwarz (23). Glycylglycine at the higher

concentrations scavenges e_{aq}^- (and OH) which in dilute solution undergo the

back-reaction $e_{aq}^- + OH \longrightarrow OH^-$ within the spur. Schuler and co-workers (24) have

recently made a detailed study of such concentration effects in aqueous

solutions of methyl chloride, which is an effective electron scavenger,

$RCl + e_{aq}^- \longrightarrow R + Cl^-$.

We note here also that the relative yields of final products derived

from the $\overset{\bullet}{C}H_2CONHCH_2COO^-$ radical, i.e. acetylglycine and aspartic acid, are

markedly dependent on glycylglycine concentration. For example, in .05$\underline{M}$

solutions, the acetylglycine and aspartic acid are produced in essentially

equal yield. However, in the 1$\underline{M}$ solution, the acetylglycine yield is almost

an order of magnitude greater than the aspartic yield. This is consistent

with the formulations of reactions 8,9 as written. At the higher solute

concentrations the radical-molecule reaction 8 is favored over the radical-

radical reaction 9.

The increase in the yield of free ammonia in the 1$\underline{M}$ solution is

accompanied by an appreciable increase in the yield of amide ammonia. Part

of this increase in the amide yield may be attributed to the fact that

$\overset{\bullet}{C}H_2CONHCH_2COO^-$ radicals in the concentrated solution are removed preferentially

through the hydrogen-abstraction step 8 to yield acetylglycine and the peptide

radical, $NH_3^+CH_2CON\overset{\bullet}{H}CHCOO^-$. Hence, the yields of both reaction 10 to give

diaminosuccinic acid and reaction 4 to give amide and carbonyl products (via

steps 6,7) are greater in the 1$\underline{M}$ solution. However, the increase in the total

carbonyl yield corresponds to $\Delta G \simeq 0.36$, whereas, the increase in the amide

yield approximates $\Delta G \simeq 0.9$. We have not been able to explain this "excess"

amide yield of $\Delta G \simeq 0.5$ simply in terms of chemistry arising from the radiation-induced step as defined by equation 1.

We note in this regard that in our earlier radiolysis studies (25,26) of the N-acetylamino acids in oxygen-free aqueous solution, we obtained evidence for involvement of excited-molecule reactions at the higher peptide concentrations. At the present time, it is not clear whether excited states of solutes in concentrated solution arise from interactions of solute with sub-excitation electrons: $RH + e^- \longrightarrow RH^* + e^-$ (27) or through charge-transfer reactions: $RH + H_2O^+ \longrightarrow RH^+ + H_2O$, $RH^+ + e^- \longrightarrow RH^*$ (28). However, the main point here is that such excited states of the peptide bond can lead to chemical change. Two major over-all reaction stoichiometries were identified in concentrated solutions of the N-acetylamino acids (25,26). For the case of glycylglycine, the analogous stoichiometries would correspond to

$$3NH_3^+CH_2CONHCH_2COO^- \longrightarrow NH_3^+CH_2CONH_2 + CH_3COO^- + 2NH_3^+CH_2CONHCHCOO^- \quad (11)$$

$$NH_3^+CH_2CONHCH_2COO^- \longrightarrow NH_3^+CH_2C(NH)OCH_2COO^- \quad (12)$$

If chemistry of type 11 were important in the production of the "excess" amide in the concentrated glycylglycine solution, we should observe both glycine amide and free acetic acid as products of the radiolysis. However, as shown in Table 1 the yield of free acetic acid from $1\underline{M}$ glycylglycine corresponds to $G \leqslant 0.1$. We conclude that reaction of type 11 is of negligible importance in this particular system. Reaction 12 may be envisaged as a simple rearrangement of the peptide bond to give the imino ester derivative
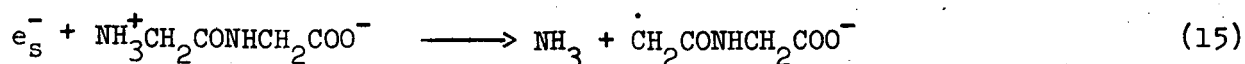
$$\sim \overset{\overset{\textstyle O}{\|}}{C}-NH\sim \longrightarrow \sim \overset{\overset{\textstyle NH}{\|}}{C}-O\sim$$
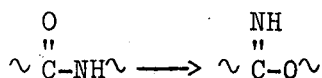
Hydrolysis of the rearrangement product of reaction 12 yields ammonia and
glycolic acid

$$2H_2O + NH_3^+CH_2C(NH)OCH_2COO^- \longrightarrow NH_3^+CH_2COO^- + NH_3 + CH_2OHCOOH \qquad (13)$$
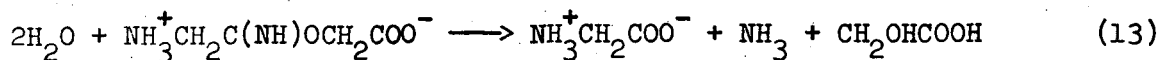
We find in Table I that glycolic acid is indeed produced in the 1M solution
with $G \simeq 0.5$ as measured after hydrolysis. (In the .05M solution, the yield
corresponds to $G \simeq 0.1$.) The ammonia derived from reaction 13 would be amide-
like in that acid or base hydrolysis is required to liberate free ammonia
from the imino ester derivative. We conclude that reaction of type 12 repre-
sents a principal source of the "excess" amide ammonia produced in the con-
centrated solution.

Solid state

As shown in Table I, we find that acetylglycine and ammonia are also
formed as major products in the radiolysis of glycylglycine in the solid state.
In fact, the specific yields of these products from solid glycylglycine and
from the concentrated glycylglycine solution are remarkably similar. We have
pointed out elsewhere (1,2) that such a result would be expected if electrons
formed in the polar glycylglycine solid escape the positive charge and subse-
quently react through reductive deamination via the analogue of reaction 2
i.e.[3]

$$NH_3^+CH_2CONHCH_2COO^- \xrightarrow{\hspace{1cm}} NH_3^+CH_2CONH\dot{C}HCOO^- + H^+ + e_s^- \qquad (14)$$

$$e_s^- + NH_3^+CH_2CONHCH_2COO^- \longrightarrow NH_3 + \dot{C}H_2CONHCH_2COO^- \qquad (15)$$

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[3]Similar reductive deamination reactions involving electrons in aqueous and solid
α-amino acid systems are discussed in reference 1.

The peptide radicals of the type formed in reaction 14 correspond to

the long-lived radical species observed in irradiated glycylglycine at room

temperature (29). The $\overset{\bullet}{C}H_2CONHCH_2COO^-$ radicals formed in reaction 15 are

removed through the equivalent of the hydrogen-abstraction reaction 8 to yield

acetylglycine and additional peptide radicals. On dissolution of the irradiated

solid in oxygen-free water, the long-lived peptide radicals formed in steps

14,8 are removed, primarily through dimerization via step 10 to yield the

diaminosuccinic acid derivative.

The stoichiometry of reactions 14,15,8 provide a basis for estimating

the yield for ion-pair production in solid glycylglycine i.e.

$G(I.P.) \cong G(NH_3)_f \cong G(CH_3CONHCH_2COOH) \cong 3.5.$

There appear to be two mechanisms for production of glyoxylic acid with

$G \cong 1$ in the radiolysis of solid glycylglycine. First, we must assume on

the basis of the aqueous studies that a fraction of the long-lived peptide

radicals $\overset{+}{N}H_3CH_2CONH\overset{\bullet}{C}HCOO^-$ present in the irradiated solid undergo the dis-

proportionation reaction 4 in parallel with the combination reaction 10 on

dissolution of the solid in water. The dehydropeptide formed in reaction 4

then undergoes hydrolysis as noted in equations 6,7 to yield carbonyl and

amide. We must also consider the direct formation of the dehydropeptide via

$$\overset{+}{N}H_3CH_2CONHCH_2COO^- \xrightarrow{\quad \ \ } \overset{+}{N}H_3CH_2CON=CHCOO^- + H_2 \qquad (16)$$
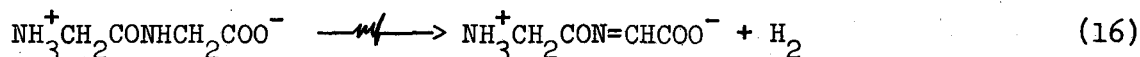
Production of the dehydropeptide function $\sim CON=C(R)\sim$ plus hydrogen in the

radiolysis of other simple peptide systems has been described in earlier

work (25). Cosgrove et al., (30) have recently estimated that reaction of

type 16 occurs in the γ-radiolysis of solid glycylglycine with $G \sim 2$. On the

basis of the present study we would say that the overall yield for dehydro-
peptide formation in reactions 4 and 16 combined cannot exceed the total
carbonyl yield viz G $\tilde{=}$ 1.3.

The production of amide and carbonyl with G $\tilde{=}$ 1.3 from solid glycyl-
glycine via steps 4,6,16 does not account for the entire yield of amide
ammonia which approximates $G(NH_3)_t$ - $G(NH_3)_f$ - 1.9. The other major source
of amide ammonia appears to be related to the radiation-induced N-O shift
described in equation 12. Such reaction leads to formation of amide-like
ammonia plus glycolic acid as the characteristic organic product. The yield
of this product in the solid glycylglycine and in the concentrated glycylgly-
cine solution is essentially the same. For the solid, the combined yield of
glycolic acid and carbonyl products corresponds to G $\tilde{=}$ 1.7 which value accounts
for a major fraction of the yield of amide ammonia.

References

(1) W. M. Garrison, Radiation chemistry of organo-nitrogen compounds, in

Current Topics In Radiation Research, vol. IV, ed. by M. Ebert and

A. Howard, North-Holland Publishing Co., Amsterdam, 1968.

(2) W. M. Garrison, Radiation-induced reactions of amino acids and peptides,

Radiation Res. Rev., 3 305-326 (1972).

(3) H. A. Makada and W. M. Garrison, Radiolytic oxidation of peptide deriva-

tives of glycine in aqueous solution, Radiation Res., 50 48-55 (1972).

(4) E. J. Conway, Microdiffusion Analysis, Crosby Lockwood and Son, London 1962.

(5) R. A. Baker, Volatile fatty acids in aqueous solution by gas-liquid

chromatography, J. Gas Chromatogr., 4 418-419 (1966).

(6) E. Lederer and M. Lederer, Chromatography, D. Van Nostrand Company Inc.,

New York 1957 pg. 184.

(7) W. M. Garrison, H. R. Haymond, W. Bennett, and S. Cole, Radiation-induced

oxidation of acetic acid-oxygen solutions. Radiation Res., 10 273-282

(1959).

(8) T. E. Friedmann and G. E. Haugen, Determination of keto acids in blood

and urine, J. Biol. Chem., 147 415-420 (1943).

(9) G. R. A. Johnson and G. Scholes, Micro determination of acetaldehyde as

its 2,4-dinitrophenylhydrazone, Analyst, 79 217-219 (1954).

(10) V. P. Calkins, Micro determination of glycolic and oxalic acids, Indust.

Eng. Chem., Anal. Ed., 15 762-763 (1943)

(11) S. Moore and W. H. Stein, Chromatography of amino acids in sulfonated

polystyrene resins., J. Biol. Chem., 192 663-681 (1951).

(12) B. M. Weeks and W. M. Garrison, Radiolysis of aqueous solutions of glycine, Radiation Res., 9 291-304 (1958).

(13) R. W. Zumwatt, K. Kuo, and C. W. Gehrke, A nanogram and picogram method for amino acid analysis by gas-phase chromatography, J. Chromatogr., 57 193-208 (1971).

(14) G. Czapski and H. A. Schwarz, The nature of the reducing species formed in water radiolysis, J. Phys. Chem., 66 471-474 (1962).

(15) E. J. Hart and J. W. Boag, Absorption spectrum of the hydrated electron, J. Am. Chem. Soc., 84 4090 (1962).

(16) A. O. Allen, Radiation yields and reactions in dilute inorganic solutions, Radiation Res., Suppl. 4 54-73 (1964).

(17) R. L. S. Willix and W. M. Garrison, Chemistry of the hydrated electron in oxygen-free solutions of amino acids, peptides and related compounds, Radiation Res., 32 452-462 (1967).

(18) W. Bennett-Corniea, H. A. Sokol, and W. M. Garrison, Reductive deamination in the radiolysis of oligopeptides in aqueous solution and in the solid state, Radiation Res., 43 257 (1970).

(19) M. Simic and E. Hayon, Reductive deamination of oligopeptides by solvated electrons in aqueous solution, Radiation Res., 48 244-255 (1971).

(20) M. D. Sevilla, Radicals formed by electron attachment to peptides, J. Phys. Chem., 74 3366-3372 (1970).

(21) W. M. Garrison, Actions of ionizing radiations on nitrogen compounds in aqueous media, Radiation Res., Suppl. 4 158-174 (1964).

(22) B. M. Weeks, S. A. Cole, and W. M. Garrison, Reactions of alanine with the reducing species formed in water radiolysis, J. Phys. Chem., 69 4131-4137 (1965).

(23) H. A. Schwarz, Applications of the spur diffusion model to the radiation chemistry of aqueous solutions, J. Phys. Chem., 73 1928-1937 (1969).

(24) T. I. Balkas, J. H. Fendler, and R. H. Schuler, Radiolysis of aqueous solutions of methyl chloride. The concentration dependence for scavenging electrons within spurs, J. Phys. Chem., 74 4497-4505 (1970).

(25) W. M. Garrison, M. E. Jayko, M. A. J. Rodgers, H. A. Sokol, and W. Bennett-Corniea, Ionization and excitation in peptide radiolysis, Adv. Chem. Ser., 81 384-396 (1968).

(26) M. A. J. Rodgers, H. A. Sokol, and W. M. Garrison, Radiolytic cleavage of the peptide main-chain in concentrated aqueous solutions: Energy level of excited-molecule intermediates, Biochem. Biophys. Res. Commun., 40 622-627 (1970).

(27) R. L. Platzman, Subexcitation electrons, Radiation Res., 2 1-5 (1955).

(28) W. H. Hamill, A model for the radiolysis of water, J. Phys. Chem., 73 1341-1347 (1969).

(29) H. C. Box, H. G. Freund, and K. Lilga, Radiation-induced parmagnetism in some simple peptides. In Free Radicals In Biological Systems, ed. by M. S. Blois, Jr. et al. Academic Press, New York, 1961.

(30) M. M. Cosgrove, M. A. Collins, R. A. Grant, and B. J. Allcock, New Zealand J. Sci., 14 599-607 (1971).

Table 1. Product Yields (G Values) In The γ-Radiolysis
of Glycylglycine In Oxygen-Free Systems

Product	Aqueous[a]		Solid[b]
	0.05M	1.0M	
Ammonia, total[c]	3.3	5.2	5.4
Ammonia, free	2.8	3.8	3.5
Acetylglycine	0.9	2.9	3.3
Acetic acid, free	<0.1	<0.1	<0.1
Glyoxylic acid	0.52	0.76	1.0
Formaldehyde	<0.10	0.22	0.30
Aspartic acid	1.1	0.30	0.1
Diaminosuccinic acid	0.8	1.7	present[d]
Glycolic acid	<0.1	0.5	0.4
Succinic acid	<0.1	<0.1	<0.1

[a]Dose, 1.4×10^{18} eV/gm solution.

[b]Dose, 2.1×10^{20} eV/gm solid.

[c]Free ammonia plus "amide" ammonia.

[d]See experimental.