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RADIATION CHEMISTRY OF GLYCYLGLYCINE IN OXYGEN-FREE SYSTEMS

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Radiation Research

RADIATION CHEMISTRY OF GLYCYLGLYCINE IN OXYGEN-FREE SYSTEMS

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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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October 1972

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 (η=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).

[1]Work performed under the auspices of the U. S. Atomic Energy Commission.

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 [$G(Fe^{3+} = 15.5$, $\varepsilon_{305} = 2180$ 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 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 hydrolyzate were identified through filter-paper chromatography (7). The quantitative 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 ∿ 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 ∿ 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)

$$H_2O \longrightarrow H_2O_2, H_2, OH, H, e^-_{aq}, H^+ \qquad (1)$$

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

$$e^-_{aq} + NH_3^+CH_2CONHCH_2COO^- \longrightarrow NH_3 + \dot{C}H_2CONHCH_2COO^- \qquad (2)$$

and that OH is removed via

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

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 .05M 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

$$NH_3^+CH_2CONH\dot{C}HCOO^- + \dot{C}H_2CONHCH_2COO^- \longrightarrow \begin{array}{l} NH_3^+CH_2CONHCHCOO^- \\ \quad\quad\quad\quad\quad\quad | \\ \quad\quad\quad\quad\quad CH_2CONHCH_2COO^- \end{array} \tag{9}$$

In the .05M glycylglycine solution, reaction 8 produces acetylalanine with $G \simeq 0.9$ and reaction 9 yields aspartic acid with $G \simeq 1.1$ as measured after hydrolysis of the irradiated solution. The peptide radicals, $NH_3^+CH_2CONH\dot{C}HCOO^-$, 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

$$2NH_3^+CH_2CONH\dot{C}HCOO^- \longrightarrow \begin{array}{l} NH_3^+CH_2CONHCHCOO^- \\ \quad\quad\quad\quad\quad\quad | \\ \quad\quad\quad\quad NH_3^+CH_2CONHCHCOO^- \end{array} \tag{10}$$

The diaminosuccinic acid observed in the hydrolyzate with $G \simeq 0.8$ 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 $\dot{C}H_2CONHCH_2COO^-$ 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 $\dot{C}H_2CONHCH_2COO^-$ radical, i.e. acetylglycine and aspartic acid, are markedly dependent on glycylglycine concentration. For example, in .05M solutions, the acetylglycine and aspartic acid are produced in essentially equal yield. However, in the 1M 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 1M 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 $\dot{C}H_2CONHCH_2COO^-$ radicals in the concentrated solution are removed preferentially through the hydrogen-abstraction step 8 to yield acetylglycine and the peptide radical, $NH_3^+CH_2CONH\dot{C}HCOO^-$. 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 1M 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

$$3NH_3^+CH_2CONHCH_2COO^- \longrightarrow NH_3^+CH_2CONH_2 + CH_3COO^- + 2NH_3^+CH_2CONH\dot{C}HCOO^- \quad (11)$$

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

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 1M 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

$$\sim \overset{O}{\overset{\|}{C}}-NH\sim \longrightarrow \sim \overset{NH}{\overset{\|}{C}}-O\sim$$

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 represents a principal source of the "excess" amide ammonia produced in the concentrated 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 subsequently react through reductive deamination via the analogue of reaction 2 i.e.[3]

$$NH_3^+CH_2CONHCH_2COO^- \rightsquigarrow NH_3^+CH_2CONH\dot{C}HCOO^- + H^+ + e_s^- \qquad (14)$$

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

[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 $\dot{C}H_2CONHCH_2COO^-$ 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. $G(I.P.) \simeq G(NH_3)_f \simeq G(CH_3CONHCH_2COOH) \simeq 3.5$.

There appear to be two mechanisms for production of glyoxylic acid with $G \simeq 1$ 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 $NH_3^+CH_2CONH\dot{C}HCOO^-$ present in the irradiated solid undergo the disproportionation 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

$$NH_3^+CH_2CONHCH_2COO^- \longrightarrow NH_3^+CH_2CON{=}CHCOO^- + H_2 \qquad (16)$$

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 dehydropeptide formation in reactions 4 and 16 combined cannot exceed the total carbonyl yield viz $G \simeq 1.3$.

The production of amide and carbonyl with $G \simeq 1.3$ from solid glycylglycine 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 glycylglycine solution is essentially the same. For the solid, the combined yield of glycolic acid and carbonyl products corresponds to $G \simeq 1.7$ which value accounts for a major fraction of the yield of amide ammonia.

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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.

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