



RESEARCH ARTICLE

Behaviour of glycine aqueous solution exposed to ionizing radiation: numerical model based on chemical kinetics

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Abstract

Glycine plays an essential role in a variety of biological and biochemical processes. As the smallest amino acid, glycine is especially important in studies of prebiotic chemistry and chemical evolution. The behaviour of glycine in aqueous solution under ionizing radiation fields is still not well understood. Understanding the reaction mechanism of glycine in an ionizing radiation environment may provide insights into the complex processes involved in prebiotic chemical synthesis. Such reaction conditions could provide clues about the environmental conditions that might favour the emergence of life. Numerical modelling based on reaction kinetics provides information on the feasibility of the reaction mechanisms. In this work, we developed a numerical model in *Python* that describes the behaviour of glycine, as prototype compound, in aqueous solution under gamma radiation. The model is based on a variety of reaction kinetics pathways that have been proposed to describe the principal reactions between glycine and the water radicals formed by ionizing radiation. The numerical results are consistent with the experiments of other researchers. We obtained similar numerical solutions from different reaction mechanisms that share the same initial reactions. The results suggest that the primary attack of water radicals on the glycine is the main factor that controls the general decay of the molar concentration of glycine and the secondary reactions do not have a strong influence, even at high doses of nearly 200 kGy. The numerical tests of the models indicate their stability with the changing initial condition of the molar concentration of glycine. This work contributes to the advancement of knowledge regarding the behaviour of glycine in aqueous solutions under ionizing radiation from a kinetic perspective. It also provides insights into their stability under conditions that are difficult to replicate in the laboratory. Finally, this work contributes to the evaluation of appropriate numerical methods for solving the system of stiff differential equations that describe the reaction mechanism of organic molecules under high radiation fields.

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Introduction

Glycine plays an essential role in biological processes. As the smallest amino acid, glycine allows for flexible links in proteins and the formation of helices. It also has several important functions in metabolic processes (Hall, 1998). The zwitterionic form of glycine ($\text{NH}_3^+\text{CH}_2\text{COO}^-$) predominates in neutral or near-neutral solutions (Fig. 1). Glycine was first detected in prebiotic experiments in the famous Miller-Urey's experiment, in which a gaseous mixture that simulated the atmosphere of the primitive Earth was subjected to electrical discharges (Miller, 1953). Miller also found aspartic acid, α and β -alanine and α -amino-n-butyric acid. This experiment was replicated and analysed with modern techniques, resulting in the detection of glycine as well as several other amino acids (Bada and Lazcano, 2003). Glycine is one of the most studied amino acids due to its physicochemical properties (Boldyreva, 2021; Rimola *et al.*, 2022), polymerization capacities (Ohara *et al.*, 2007; Kitadai, 2014), its interactions with minerals (Kitadai *et al.*, 2017; Pedreira-Segade *et al.*, 2019; Baú *et al.*, 2021), the formation of fluid inclusions during crystallization (Angeles-Camacho *et al.*, 2020) and applications in a range of fields in science and technology (Hall, 1998; Boldyreva, 2021).

Glycine and other organic molecules (including aromatic hydrocarbons, alcohols, ethers, amines and amino acids) were detected in comets for the first time in the analysis of samples that impacted in aerogel collected by the Stardust spacecraft on the Comet 81/Wild 2 (Sandford *et al.*, 2006). The detection of organic molecules on comets supports the theory that extraterrestrial bodies (e.g. comets and asteroids) played an important role in prebiotic chemistry, potentially leading to the origin of life (Chyba and Sagan, 1992).

The effects of ionizing radiation on glycine in aqueous solution systems have been studied by several researchers since the mid-twentieth century (Dale *et al.*, 1949; Stein and Weiss, 1949; Neta *et al.*, 1969). A wide variety of molecules are produced by irradiation, such as amino acids, carboxylic acids and polymers (Maxwell *et al.*, 1954; Weeks and Garrison, 1958; Draganić *et al.*, 1985). The reaction mechanism that governs this process is not fully understood due to the many possible intermediate reactions. This topic has been extensively studied by several researchers, with many proposed possible reaction pathways (Maxwell *et al.*, 1955; Garrison and Weeks, 1956; Weeks and Garrison, 1958; Draganić *et al.*, 1985). In any case, glycine in aqueous solution under ionizing radiation has many chain reactions and yields a large variety of radiolysis products.

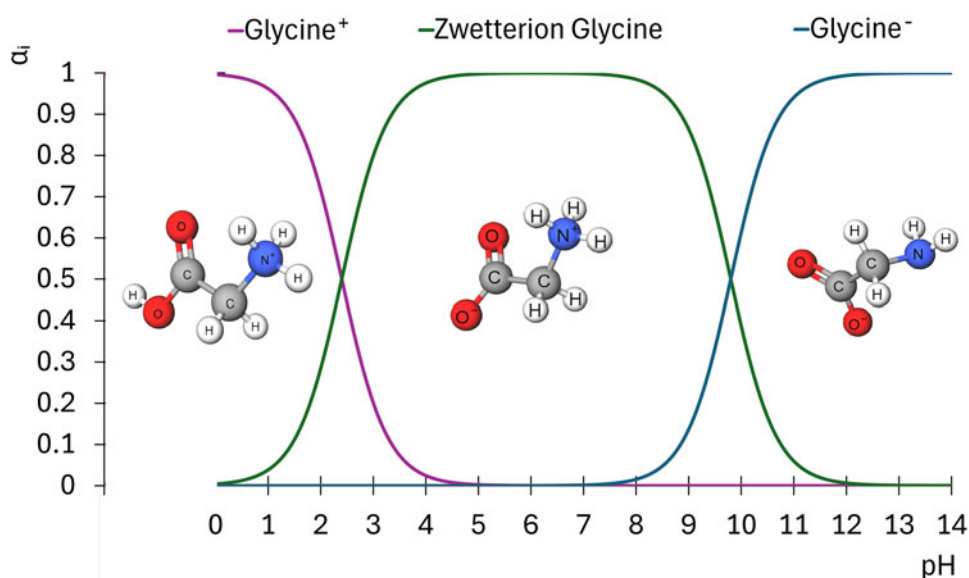


Figure 1. Species diagram for glycine depending on pH. Zwitterionic form of glycine is present at neutral and near-neutral pH.

The numerical models have been developed as an alternative to understand different processes about the radiation-induced reactions (Samuel and Magee, 1953; Dewhurst *et al.*, 1954; Kuppermann and Belford, 1962; Schwarz, 1969). The numerical approximations can be very complex, with many variables such as the diffusion of the molecules, energy loss, the geometry, the total media volume, biological damage, etc. (Barilla *et al.*, 2008; Fasso *et al.*, 2011; McMahon *et al.*, 2013; Dobrzyński *et al.*, 2019). In addition, some of these types of models require specialized computing equipment to obtain numerical solutions. In the case of a numerical method simpler and manageable with a standard computer, some researchers have focused on the mass balance of the reactions with organic molecules (Cruz-Castañeda *et al.*, 2015; Rivera *et al.*, 2018; Paredes-Arriaga *et al.*, 2024a), at different temperatures (Martínez *et al.*, 2004; Sánchez-Mejorada *et al.*, 2008; Rivera *et al.*, 2017; Paredes Arriaga *et al.*, 2023), at different pH values (Horne *et al.*, 2020; Paredes-Arriaga *et al.*, 2024b) or using artificial intelligence methods (Rivera *et al.*, 2016, 2020).

In this work, we studied the possible and probable pathways of reaction mechanisms for the first stages of glycine in aqueous solution under ionizing radiation, as a prototype molecule that can be extended to other compounds relevant in prebiotic chemistry. We developed a numerical model based on two chemical reaction mechanisms to approximate a solution that reproduces the behaviour of glycine based on the experimental work of Draganić *et al.* (1985). Our numerical model is based on a system of coupled differential equations, which are more difficult to solve the more variables there are. In a system based on reaction kinetics, a larger number of molecules implies greater difficulty finding a numerical solution. Solving a reaction involving more than 15 molecules is a substantial numerical challenge. This work has three main objectives: (1) Validate the feasibility of the proposed reaction mechanisms using numerical methods with previous experimental results. An infeasible reaction mechanism could not ever be simulated in agreement with experimental data. (2) Selection of a parametric configuration of an appropriate numerical method for solving the system of stiff differential equations describing the proposed reaction mechanism. (3) Developing new numerical methods is an alternative approach to problems in prebiotic chemistry, astrobiology, and radiation chemistry. Providing insights into the complex processes of organic molecules under extreme environments with high radiation doses and offering hints about the environmental conditions that might favour the emergence of life.

Methods

The experimental samples modelled were an aqueous solution of 0.1 mol L⁻¹ glycine at pH 6.2, oxygen-free, exposed to radioactive cobalt sources and dose rates of 0.1 Mrad h⁻¹, equivalent to 1000 Gy h⁻¹. The higher-dose irradiation was 200 kGy. All experimental values are determined from the work by Draganić *et al.* (1985). Standard temperature and pressure conditions are used for all the experiments.

Each reaction mechanism was ensembled based on a literature review of experiments involving aqueous glycine irradiated with gamma-radiation. The reaction mechanisms were reinterpreted as a system of nonlinear differential equations, with one equation for each molecule in the chemical reactions. For example, if the reaction mechanism has 15 chemical species, then the system of nonlinear differential equations comprises 15 differential equations that are solved simultaneously (Paredes-Arriaga *et al.*, 2024a). Equation (1) has three terms: the positive part represents the formation of molecules by this reaction, the negative part represents the destruction of molecules for the reaction, and $f_i(\text{Id})$ is a function that simulates the radiation source (Martínez *et al.*, 2004), developed in equation (2).

$$\frac{dX_i(t)}{dt} = f_i + \sum_{m=0}^N \sum_{n=0}^N k_{m,n}^{(i)} X_m(t) X_n(t) - X_i(t) \sum_{j=0}^N k_{i,j}^{(i)} X_j(t), \quad (1)$$

$$f_i(\text{Id}) = \frac{6.2 \times 10^{11}}{3.6 \text{ AN}} \frac{M_i}{M_{\text{H}_2\text{O}}} G_i [\text{Id} \times (6 \times 10^3)], \quad (2)$$

where X_i , X_j , X_m and X_n are the molar concentrations of i -species at time t , $k_{ij}^{(i)}$ and $k_{m,n}^{(i)}$ are the rate constants between the i and j species, and m and n species, respectively. In the source term $[f_i(\text{Id})]$, AN is Avogadro's number, M_i is the molecular mass of i chemical species, $M_{\text{H}_2\text{O}}$ is the molecular mass of water, G_i is the radiochemical yield of the i species and Id is the dose intensity in Gy min^{-1} . The radiochemical yields (number of molecules formed or destroyed by 100 eV, or 1 molecule/100 eV = $0.1036 \mu\text{mol J}^{-1}$) of water radicals produced by gamma radiation are: $\bullet\text{OH} = 0.28 \mu\text{mol J}^{-1}$, $\text{H}\bullet = 0.28 \mu\text{mol J}^{-1}$, $e_{\text{aq}}^- = 0.062 \mu\text{mol J}^{-1}$ (Spinks and Woods, 1990; Le Caër, 2011). The source terms apply only to the simulation of the water radicals formed by gamma radiation. Thus, they are written only for $\bullet\text{OH}$, $\text{H}\bullet$ and e_{aq}^- .

To compute the coupled nonlinear differential equation system, we built a program in *Python* (3.7.9) using the *SciPy* library (Virtanen *et al.*, 2020), the *solve_ivp* module, with the *Radau* method and the *BDF* method. The *Radau* method uses an implicit Runge–Kutta method of fifth-order from of the *Radau* IIA family (Hairer and Wanner, 1996). The error is controlled with a third-order accurate embedded formula. A cubic polynomial that satisfies the collocation conditions is used for the dense output. The *BDF* method uses an implicit multistep method of variable order (1–5) with a backward differentiation formula for the derivative approximation (Harris *et al.*, 2020). The general algorithm and full code are available at https://github.com/A-Paredes-Arriaga/Chemical-kinetics_EDOs_2-Glycine. Finally, the root mean square error (RMSE) and the R^2 between numerical model and the experimental data were calculated for statistical support. The sum and mean of the residuals between the experimental data and numerical solutions were also calculated.

Reaction mechanisms

We use two reaction mechanisms that structure the numerical model on the behaviour of glycine aqueous solution under gamma radiation.

Short reaction mechanism: This mechanism was proposed on the descriptions of Spinks and Woods (1990) based on previous work (Dale *et al.*, 1949; Stein and Weiss, 1949; Maxwell *et al.*, 1954; Garrison and Weeks, 1956; Weeks and Garrison, 1958; Willix and Garrison, 1967). Table 1 describes the primary attack of the water radicals on glycine and Table 2 describes some secondary reactions.

Long reaction mechanism: This mechanism was taken from the work of Draganić *et al.* (1985); they proposed it to explain the formation of different products detected. Consequently, this mechanism has more reactions and products (Table 3).

Results and discussion

Two reaction mechanisms were modelled. The aim was to compare the general computational solutions for mechanisms with different numbers of reactions: A short one with seven reactions and a

Table 1. Initial attack of water radicals on the glycine in aqueous solution at neutral and near-neutral pH

Reactives		Products	k (s^{-1})	Reaction number
H_2O	$\xrightarrow{\gamma\text{-rad}}$	$\bullet\text{OH}$, e_{aq}^- , $\text{H}\bullet$		{1}
$\text{NH}_3^+\text{CH}_2\text{COO}^- + \bullet\text{OH}$ (glycine)	$\xrightarrow{k_1}$	$\text{NH}_3^+\text{C}\bullet\text{HCOO}^- + \text{H}_2\text{O}$	$k_1 = 8.8 \times 10^3$	{2}
$\text{NH}_3^+\text{CH}_2\text{COO}^- + \text{H}\bullet$ (glycine)	$\xrightarrow{k_2}$	$\text{NH}_3^+\text{C}\bullet\text{HCOO}^- + \text{H}_2$	$k_2 = 77$	{3}
$\text{NH}_3^+\text{CH}_2\text{COO}^- + e_{\text{aq}}^-$ (glycine)	$\xrightarrow{k_3}$	$\text{NH}_3^+ + \text{C}\bullet\text{H}_2\text{COO}^-$ (ammonia) (acetoxy $^{\ominus}$ rad)	$k_3 = 1.7 \times 10^4$	{4a}
	\rightarrow	$\bullet\text{NH}_2^+\text{CH}_2\text{COO}^-$		{4b}

Table 2. Secondary reactions of the primary glycine products

Reactives		Products	Reaction number
$2 \bullet \text{NH}_2^+ \text{CH}_2 \text{COO}^-$	$\xrightarrow{k_n}$	$(\text{NH}_2^+ = \text{CHCOO}^-) + \text{NH}_3^+ \text{CH}_2 \text{COO}^-$ (intermediate iminoacetic acid) (glycine)	{5}
$\text{NH}_3^+ \text{C} \bullet \text{HCOO}^- + \text{C} \bullet \text{H}_2 \text{COO}^-$ (acetoxyl ⁻ rad)	$\xrightarrow{k_n}$	$(\text{NH}_2^+ = \text{CHCOO}^-) + \text{CH}_3 \text{COO}^-$ (intermediate iminoacetic acid) (acetic acid)	{6}
$(\text{NH}_2^+ = \text{CHCOO}^-) + \text{H}_2 \text{O}$ (intermediate iminoacetic acid)	$\xrightarrow{k_n}$	$\text{NH}_4^+ + \text{HC}(= \text{O}) \text{COO}^-$ (ammonium cation) (glyoxylic acid)	{7a}
	$\xrightarrow{k_n}$	$\text{NH}_3^+ + \text{HCHO} + \text{CO}_2$ (ammonia) (formaldehyde) (carbon dioxide)	{7b}

long one with 18 reactions. Both systems only modelled the first stage of the radiation-induced glycine reactions.

When an aqueous solution of glycine is irradiated with ionizing radiation, the zwitterion glycine reacts with the primary water radicals ($\bullet \text{OH}$, $\text{H} \bullet$ and e_{aq}^-) to form ammonia, glycine radicals and other unstable species (reactions 1–4) (Spinks and Woods, 1990). In the short reaction mechanism, after the primary attack of water radicals, each species of glycine radical can undergo secondary reactions to form acids, such as acetic acid and glyoxylic acid (reactions 6 and 7a). The interaction of two $\bullet \text{NH}_2^+ \text{CH}_2 \text{COO}^-$ radicals results in the regeneration of glycine and the formation of the intermediate iminoacetic acid (reaction 5) (Spinks and Woods, 1990). For reaction 4, which does not have a dominant product, we assumed that half of the reactions formed ammonia and acetoxyl⁻ radical, and the other half formed the intermediate $\bullet \text{NH}_2^+ \text{CH}_2 \text{COO}^-$ radical. Reaction 7 has two probable pathways, with the dominant reaction (reaction 7a) producing ammonium cation and glyoxylic acid, while a secondary reaction (reaction 7b) produces ammonia, formaldehyde and carbon dioxide. In this case, reaction 7a occurs 80% of the time and 7b 20% of the time.

The complete reaction mechanism was rewritten as a system of coupled differential equations according to equations (1) and (2). It used the notation k_n for the unknown rate constants. Glycine is abbreviated as ‘Gly’.

$$\frac{dX_{\bullet \text{OH}}(t)}{dt} = f_{\bullet \text{OH}} - k_1 X_{\text{Gly}}(t) X_{\bullet \text{OH}}(t) \quad (3)$$

$$\frac{dX_{\text{H} \bullet}(t)}{dt} = f_{\text{H} \bullet} - k_2 X_{\text{Gly}}(t) X_{\text{H} \bullet}(t) \quad (4)$$

$$\frac{dX_{\text{e}_{\text{aq}}^-}(t)}{dt} = f_{\text{e}_{\text{aq}}^-} - k_3 X_{\text{Gly}}(t) X_{\text{e}_{\text{aq}}^-}(t) \quad (5)$$

$$\begin{aligned} \frac{dX_{\text{Gly}}(t)}{dt} = & -k_1 X_{\text{Gly}}(t) X_{\bullet \text{OH}}(t) - k_2 X_{\text{Gly}}(t) X_{\text{H} \bullet}(t) \\ & - k_3 X_{\text{Gly}}(t) X_{\text{e}_{\text{aq}}^-}(t) + k_n X_{\bullet \text{NH}_2^+ \text{CH}_2 \text{COO}^-}(t) / 2 \end{aligned} \quad (6)$$

$$\begin{aligned} \frac{dX_{\text{NH}_3^+ \text{C} \bullet \text{HCOO}^-}(t)}{dt} = & +k_1 X_{\text{Gly}}(t) X_{\bullet \text{OH}}(t) + k_2 X_{\text{Gly}}(t) X_{\text{H} \bullet}(t) \\ & - k_n X_{\text{NH}_3^+ \text{C} \bullet \text{HCOO}^-}(t) X_{\text{C} \bullet \text{H}_2 \text{COO}^-}(t) \end{aligned} \quad (7)$$

Table 3. Reaction mechanism of glycine under gamma radiation

Reactives		Products	Reaction number
H ₂ O	$\xrightarrow{\gamma\text{-rad}}$	$\bullet\text{OH}, e_{\text{aq}}^-, \text{H}\bullet$	{1}
NH ₃ ⁺ CH ₂ COO ⁻ + $\bullet\text{OH}$ (glycine)	$\xrightarrow{k_1}$	NH ₃ ⁺ C \bullet HCOO ⁻ + H ₂ O	{2}
NH ₃ ⁺ CH ₂ COO ⁻ + H \bullet (glycine)	$\xrightarrow{k_2}$	$\bullet\text{NH}_2^+\text{CH}_2\text{COO}^- + \text{H}_2\text{O}$	{8}
NH ₃ ⁺ CH ₂ COO ⁻ + e _{aq} ⁻ (glycine)	$\xrightarrow{k_3}$	NH ₃ ⁺ C \bullet HCOO ⁻ + H ₂	{3}
	$\xrightarrow{k_3}$	$\bullet\text{NH}_2^+\text{CH}_2\text{COO}^- + \text{H}_2$	{9}
	$\xrightarrow{k_3}$	NH ₃ ⁺ + C \bullet H ₂ COO ⁻ (ammonia) (acetoxyl ⁻ rad)	{4a}
	\rightarrow	H + NH ₂ ⁺ CH ₂ COO ⁻	{4b}
	\rightarrow	H + OH ⁻ + NH ₃ ⁺ CH ₂ C \bullet O	{10}
2 NH ₃ ⁺ C \bullet HCOO ⁻	$\xrightarrow{k_n}$	(NH ₂ ⁺ =CHCOO ⁻) + NH ₃ ⁺ CH ₂ COO ⁻ (int. iminoacetic acid) (glycine)	{11a}
	$\xrightarrow{k_n}$	NH ₃ ⁺ CHCOO ⁻	{11b}
		 NH ₃ ⁺ CHCOO ⁻ (Diaminosuccinic acid)	
NH ₃ ⁺ C \bullet HCOO ⁻ + C \bullet H ₂ COO ⁻ (acetoxyl ⁻ rad)	$\xrightarrow{k_n}$	(NH ₂ ⁺ =CHCOO ⁻) + CH ₃ COO ⁻ (intermediate iminoacetic acid) (acetic acid)	{12a}
	$\xrightarrow{k_n}$	NH ₃ ⁺ CHCOO ⁻	{12b}
		 CH ₂ COO ⁻ (aspartic acid)	
NH ₂ ⁺ =CHCOO ⁻ + H ₂ O (intermediate iminoacetic acid)	$\xrightarrow{k_n}$	NH ₄ ⁺ + HC(=O)COO ⁻ (ammonium cation) (glyoxylic acid)	{13a}
	$\xrightarrow{k_n}$	NH ₃ ⁺ + HC \bullet (OH)COO ⁻ (ammonia)	{13b}
	$\xrightarrow{k_n}$	NH ₄ ⁺ + HCHO + CO ₂ (ammonium cation) (formaldehyde)	{13c}
C \bullet H ₂ COO ⁻ + $\bullet\text{NH}_2^+\text{CH}_2\text{COO}^-$ (acetoxyl ⁻ rad)	$\xrightarrow{k_n}$	NH ₂ ⁺ (CH ₂ COO ⁻) ₂ (iminodiacetic acid)	{14}
HC \bullet (OH)COO ⁻ + NH ₃ ⁺ C \bullet HCOO ⁻	$\xrightarrow{k_n}$	NH ₃ ⁺ CHCOO ⁻	{15}
		 HC(OH)COO ⁻ (OH aspartic acid)	
HC \bullet (OH)COO ⁻ + NH ₃ ⁺ CH ₂ COO ⁻ (glycine)	$\xrightarrow{k_n}$	CH ₂ (OH)COO ⁻ + NH ₃ ⁺ C \bullet HCOO ⁻	{16}
NH ₃ ⁺ C \bullet H ₂ + NH ₃ ⁺ CH ₂ COO ⁻ (glycine)	$\xrightarrow{k_n}$	CH ₃ NH ₃ ⁺ + NH ₃ ⁺ C \bullet HCOO ⁻ (methylamine)	{17}
NH ₃ ⁺ C \bullet H ₂ + C \bullet H ₂ COO ⁻ (acetoxyl ⁻ rad)	$\xrightarrow{k_n}$	NH ₃ ⁺ CH ₂ CH ₂ COO ⁻ (Alanine)	{18}

Adapted from the work of Draganić *et al.* (1985).

$$\frac{dX_{\text{H}_2\text{O}}(t)}{dt} = +k_1X_{\text{Gly}}(t)X_{\bullet\text{OH}}(t) - k_nX_{(\text{NH}_2^+=\text{CHCOO}^-)}(t)X_{\text{H}_2\text{O}}(t) \quad (8)$$

$$\frac{dX_{\text{H}_2}(t)}{dt} = +k_2X_{\text{Gly}}(t)X_{\text{H}\bullet}(t) \quad (9)$$

$$\frac{dX_{\text{NH}_3^+}(t)}{dt} = +[k_3 X_{\text{Gly}}(t) X_{e_{\text{aq}}^-}(t)] \times 0.5 + [k_n X_{(\text{NH}_2^+ = \text{CHCOO}^-)}(t) X_{\text{H}_2\text{O}}(t)] \times 0.2 \quad (10)$$

$$\frac{dX_{\text{C}^* \text{H}_2 \text{COO}^-}(t)}{dt} = +[k_3 X_{\text{Gly}}(t) X_{e_{\text{aq}}^-}(t)] \times 0.5 - k_n X_{\text{NH}_3^+ \text{C}^* \text{HCOO}^-}(t) X_{\text{C}^* \text{H}_2 \text{COO}^-}(t) \quad (11)$$

$$\frac{dX_{\text{NH}_2^+ \text{CH}_2 \text{COO}^-}(t)}{dt} = +[k_3 X_{\text{Gly}}(t) X_{e_{\text{aq}}^-}(t)] \times 0.5 - k_n X_{\text{NH}_2^+ \text{CH}_2 \text{COO}^-}(t) \quad (12)$$

$$\begin{aligned} \frac{dX_{(\text{NH}_2^+ = \text{CHCOO}^-)}(t)}{dt} &= +k_n X_{\text{NH}_2^+ \text{CH}_2 \text{COO}^-}(t)/2 + k_n X_{\text{NH}_3^+ \text{C}^* \text{HCOO}^-}(t) X_{\text{C}^* \text{H}_2 \text{COO}^-}(t) \\ &- k_n X_{(\text{NH}_2^+ = \text{CHCOO}^-)}(t) X_{\text{H}_2\text{O}}(t) \end{aligned} \quad (13)$$

$$\frac{dX_{\text{CH}_3 \text{COO}^-}(t)}{dt} = +k_n X_{\text{NH}_3^+ \text{C}^* \text{HCOO}^-}(t) X_{\text{C}^* \text{H}_2 \text{COO}^-}(t) \quad (14)$$

$$\frac{dX_{\text{NH}_4^+}(t)}{dt} = +[k_n X_{(\text{NH}_2^+ = \text{CHCOO}^-)}(t) X_{\text{H}_2\text{O}}(t)] \times 0.8 \quad (15)$$

$$\frac{dX_{\text{HC}(=O) \text{COO}^-}(t)}{dt} = +[k_n X_{(\text{NH}_2^+ = \text{CHCOO}^-)}(t) X_{\text{H}_2\text{O}}(t)] \times 0.8 \quad (16)$$

$$\frac{dX_{\text{HCHO}}(t)}{dt} = +[k_n X_{(\text{NH}_2^+ = \text{CHCOO}^-)}(t) X_{\text{H}_2\text{O}}(t)] \times 0.2 \quad (17)$$

$$\frac{dX_{\text{CO}_2}(t)}{dt} = +[k_n X_{(\text{NH}_2^+ = \text{CHCOO}^-)}(t) X_{\text{H}_2\text{O}}(t)] \times 0.2 \quad (18)$$

The long reaction mechanism starts with the primary attack of water radicals (OH^* , H^*) and solvated electron (e_{aq}^-) but has more proposed products (reactions 8–10) than reaction 2–4. Each reaction intermediary will react to form new chemical species of acids and amino acids.

There are large differences between both reaction mechanisms; most significantly, the number of reactions and chemical species involved. The short mechanism with seven reactions and 17 molecules is challenging from a numerical point of view because this type of problem (stiff problem) is very sensitive to initial conditions. Hence, the long reaction mechanism with 12 reactions, some with multiple probable pathways and more than 30 molecules, can easily generate unstable solutions, giving a smaller stability window. It is important to note that this long reaction mechanism is the largest system solved compared to previous work (Martínez *et al.*, 2004; Negron-Mendoza *et al.*, 2012; Rivera *et al.*, 2017, 2018; Paredes Arriaga *et al.*, 2023; Paredes-Arriaga *et al.*, 2024a, 2024b). The numerical solutions of both reaction mechanisms show the continuous decay of the molar concentration of glycine, which agrees with the experimental data (Fig. 2).

The difference between the molar concentration of glycine from the numerical solutions of the two reaction mechanisms is less than 1%, equivalent to 0.001 mol L^{-1} (Fig. 2 and Table 1). The statistical analysis of the experimental results of Draganić *et al.* (1985), and each reaction mechanism shows good agreement, with Pearson and R^2 coefficients greater than 0.96. Reaction mechanisms short and long have small RMSEs, equivalent to 3.28 and 3.46%, respectively. Long mechanism presents a larger residual sum (5.41%) and residual mean (1.35%) than mechanism short for variations generated by differences in the reaction mechanism. Also, each parameter was under the acceptable value (Table 4). The numerical results are similar but not identical, indicating that the behaviour of the two mechanisms presented is different (Table 5).

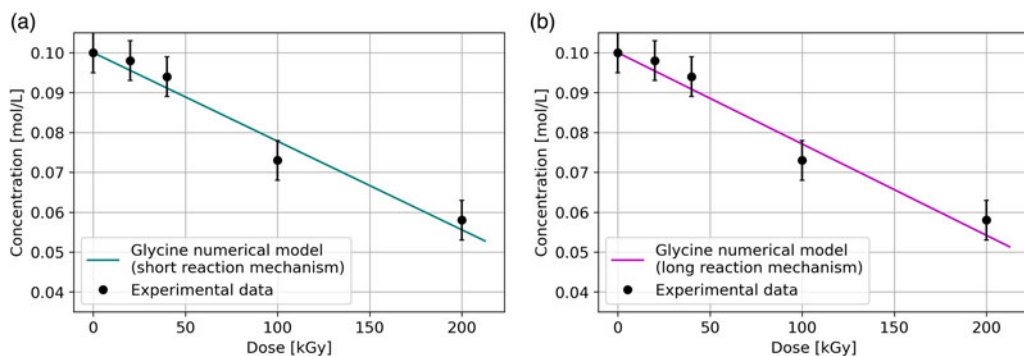


Figure 2. Glycine aqueous solution under high gamma radiation fields, from 0 to 200 kGy. (A) Green line is the numerical solution based on the chemical reactions compiled by Spinks and Woods (1990). (B) Pink line is the numerical solution based on the chemical reaction mechanism proposed by Draganić *et al.* (1985). The dots are the experimental data obtained by Draganić *et al.* (1985).

Table 4. Decay data of the molar concentration of glycine in aqueous solution under gamma radiation

Dose (kGy)	Draganić <i>et al.</i> (1985) Gly [mol L ⁻¹]	Mechanism 1 (short) Gly [mol L ⁻¹]	Mechanism 2 (long) Gly [mol L ⁻¹]
0	0.1	0.1	0.1
20	0.098	0.0956	0.0954
40	0.094	0.0911	0.0908
100	0.073	0.0778	0.0771
200	0.058	0.0556	0.0542

Experimental data and both reaction mechanisms exhibit a constant decay, as plotted in Fig. 2(A) and (B).

Table 5. Statistical analysis of the experimental results and their relationship to each numerically computed solution, as well as their percentage equivalent

	Mechanism 1	%	Mechanism 2	%
Pearson	0.9806		0.9805	
R^2	0.9615		0.9615	
RMSE	0.0033	3.28	0.0035	3.46
Residual sum	0.0029	2.94	0.0054	5.41
Residual mean	0.0007	0.74	0.0014	1.35

Only the three initial rate constants are known, corresponding to the primary attack of water radicals. With these rate constants, it is possible to model the most general behaviour of glycine in an aqueous solution. However, it is impossible to give information about the behaviour of any product of the system, because the primary products are unstable chemical species.

Given the construction of the nonlinear differential equations system, it is necessary to assign a rate constant as a part of the initial conditions. The numerical model cannot begin to compute a solution without a rate constant associated for each reaction. The three known constants have an order of magnitude between 1.0×10^1 and $1.0 \times 10^4 \text{ s}^{-1}$; thus, in radiation chemistry they can be considered slow reactions. We assumed that the secondary reactions are equally slow, around $\sim k_n = 1.0 \times 10^4 \text{ s}^{-1}$, and

have the same rate constant. The results in Fig. 2(A) and (B) and Table 4 were calculated using this constant as the initial condition for reactions 5–7.

To study the sensitivity of the model to changes in the initial conditions (k_n), we vary the order of magnitude of k_n in a wide range. The BDF method provides the most stable numerical solution. In the model of the short reaction mechanism, the rate constant (k_n) can vary between 1.0×10^1 and $1.0 \times 10^{10} \text{ s}^{-1}$ without causing significant changes in the numerical calculation of the decay of the molar concentration of glycine; indeed, they give the same result to the seventh decimal. This suggests that the primary attack of water radicals lead the decay of the molar concentration of glycine by gamma radiation. The model of the long reaction mechanism has a small stability window for the rate constant and shows the same solutions from $k_n = 1.0 \times 10^2$ to $k_n = 1.0 \times 10^9 \text{ s}^{-1}$. The solutions with a lower constant become unstable, and the system shows no solution with a higher constant. With the *Radau* method it is not possible to get numerical solutions of the short reaction mechanism when $k_n \geq 1.0 \times 10^6 \text{ s}^{-1}$.

We varied the initial concentration of both reaction mechanisms to evaluate the numerical stability of the calculated solutions. Each model reached stable solutions when the initial concentration was increased to 1 mol L^{-1} . The short reaction mechanism generates stable solutions when the initial concentration is less than 0.01 mol L^{-1} (Fig. 3(Aa–e)), however, the longer reaction mechanism quickly becomes unstable and collapses before 500 Gy (Fig. 3(Ba–e)). This behaviour is likely due to the extensive amount of chains reaction in this reaction mechanism.

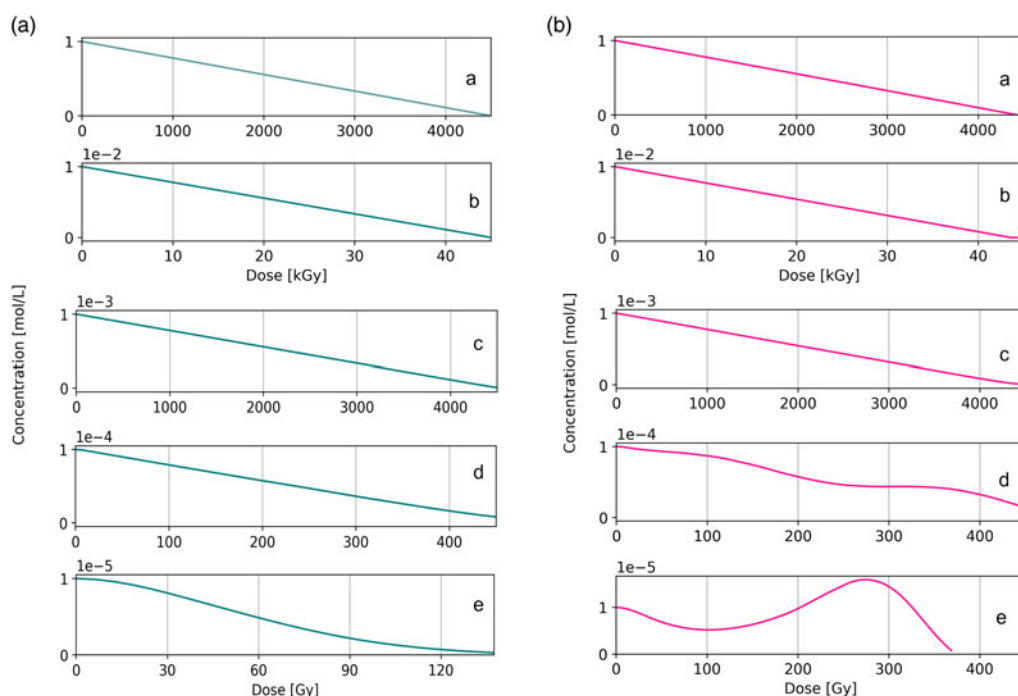


Figure 3. The tolerance of numerical model to variations in initial concentration. (A) The short reaction mechanism generates stable solutions even when the initial concentration is varied by ± 1 order of magnitude (a, b). The solutions continue to be stable when the initial glycine concentration is reduced to 1×10^{-3} , 1×10^{-4} and $1 \times 10^{-5} \text{ mol L}^{-1}$ (c, d, e). (B) The long reaction mechanisms generate stable solutions when the initial glycine concentration is increased to 1 mol L^{-1} (a) and decreased to 1×10^{-2} and $1 \times 10^{-3} \text{ mol L}^{-1}$ (b, c); however, the solutions become unstable at $1 \times 10^{-5} \text{ mol L}^{-1}$ (e). Note that the doses for stable solutions are from 0 to 4000 kGy, and when the system becomes unstable occurs at less than 500 Gy.

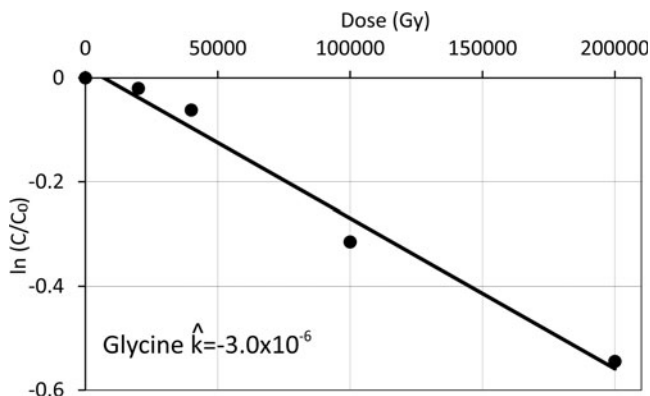


Figure 4. Dose constant calculation for glycine in aqueous solution (0.1 mol L^{-1}).

Given the stability and relative simplicity of short reaction mechanism, the numerical model allowed the calculation of solutions for low-concentration systems. Glycine tolerance was reduced proportionally from its initial concentration. At $1 \times 10^{-3} \text{ mol L}^{-1}$, the glycine is completely lost before 5 kGy (Fig. 3(Ac)); with $1 \times 10^{-4} \text{ mol L}^{-1}$, the glycine is completely lost before 500 Gy (Fig. 4(Ad)); and with $1 \times 10^{-5} \text{ mol L}^{-1}$, its molar concentration decreases to almost zero at 150 Gy (Fig. 3(Ae)). These approximations assumed that the reaction mechanism is the same as that of a system with an initial concentration of 0.1 mol L^{-1} . These results are only a numerical approximation; the experimental comparison will be a future work.

We wish to emphasize that, based on the results shown here, models based on a system on coupled differential equations should aim to work with as few variables as possible, keeping the model simple but not simplistic. Here, we recommend working with the short reaction pathway if allowed by the research question; this is because the stability window in terms of the initial conditions is higher, the total number of known and unknown variables is fewer, and the system requires less computational resources to generate solutions.

From the experimental data, the dose constant (\hat{k}) of this molecule can be calculated as:

$$\ln\left(\frac{C}{C_0}\right) = -\hat{k}D \Rightarrow \hat{k} = -\ln\left(\frac{C}{C_0}\right)/D, \quad (19)$$

where C is the concentration, C_0 is the initial concentration, D is the applied dose (in Gy) and \hat{k} is the dose constant (Gy^{-1}). The dose constant for glycine in aqueous solution (0.1 mol L^{-1}) is $\hat{k} = 3.0 \times 10^{-6}$ (Fig. 4). This constant gives insight into the degradation of the molecule and expresses the reaction kinetics as a pseudo-first-order reaction, but it is only descriptive (Criquet and Karpel Vel Leitner, 2011, 2012). The experimental behaviour of glycine degradation under gamma radiation as a pseudo-first-order reaction allows our numerical model to express the reactions as pseudo-first-order equations. For this reason, the model based on a coupled differential equation system has only reactions of this rate order (equations (3)–(18)).

Comments and conclusions

The radiolysis of glycine in aqueous solutions yields many products, including carboxylic acids and amino acids. Computational models based on two reaction mechanisms presented in this work provide insights into the main factors that control the general behaviour of glycine under gamma radiation. In this case, the primary attack of the water radicals dominates the decay of molar concentration of glycine. We can give information about the molar concentration of glycine at different doses and concentrations, but we cannot give information about the products or reaction intermediates because these rate constants are unknown.

It is important to note that the results presented only reproduce the first stages of radiolysis. High-dose irradiation also produces high-molecular-weight molecules, for which the reaction mechanisms are not defined. In addition, all reaction mechanisms and numerical solutions compiled in this work are valid only at near-neutral pH. The rate constants and reaction mechanisms may be altered in strongly acidic or strongly basic solutions (Stein and Weiss, 1949). All results presented were developed at a near-neutral pH and at standard temperature and pressure conditions, these conditions have been defined in advance by the experimental part. The variation of these parameters or the initial concentration may change the experimental results in terms of the molar concentration of reactants and products. The change in environmental conditions would imply a change of the simulation. For example, the species formed by water radiolysis act as acid/base pair, such as $\text{H}^\bullet/\text{e}_{\text{aq}}^-$, which are regulated by the proton concentration; this change is contemplated in the source term of equation (2). In addition, in an acidic or basic simulation, glycine is converted to glycinium or glycinate, respectively. The reaction mechanism and the radiolysis products would change. The acid/base pair of formic acid and formate ion shows this behaviour. The radiolysis products are different for irradiation of pure formic acid, pure formate or a mixture of both molecules. The products also change with the concentration (Paredes-Arriaga *et al.*, 2024b). On the other hand, the temperature affects qualitatively the yields of the reaction due to the diffusion of the species at low temperature. At higher temperatures up to 75° C there is not a notable effect in other molecules, like succinic acid (Negrón-Mendoza and Ponnampuram, 1982), and probably this is also for glycine. It would be part of future work, both in the experimental part and in the numerical part.

The numerical solutions validate the reaction mechanism of the primary reactions of glycine with water radicals. The possibility of approximating the glycine decomposition rate in extreme scenarios with different molar concentrations, radiation doses and dose rates will help to support hypotheses about the behaviour of organic molecules under primitive or extraterrestrial environments, especially since glycine is a precursor of other biologically important molecules. This work contributes to the understanding of the possible and probable pathways that glycine can follow in a variety of prebiotic environments with water near-neutral pH and exposed to ionizing radiation, such as near-neutral lakes, some parts of hydrothermal spring systems, glacial brines or shallow freshwater.

Finally, the numerical models presented in this work can have a wide scope for future applications in various fields of science and technology. The solutions of systems of strongly coupled nonlinear differential equations, specifically designed to simulate the behaviour of organic and inorganic chemical species under ionizing radiation, could have many applications beyond prebiotic chemistry. Some potential examples would be: in topics of radiation chemistry and radiochemistry, astrobiology and planetary science; in environmental chemistry to predict the degradation of pollutants in water bodies or in nuclear waste management; in climate change to simulate the effects of cosmic radiation on atmospheric chemical species.

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