

Glycine Decarboxylation: The Free Radical Mechanism

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Abstract: Radiation chemical methods were used to investigate the reactions of glycine anions, $\text{H}_2\text{NCH}_2\text{CO}_2^-$ (Gly^-), with $\cdot\text{OH}$, $(\text{CH}_3)_2\text{C}\cdot\text{OH}$, and $\cdot\text{CH}_3$ radicals. A major and most significant product from all of these processes is CO_2 . Pulse-radiolysis revealed that the initial step in the $\cdot\text{OH}$ -induced mechanism is oxidation of the amino group, producing $^+\text{H}_2\text{N}\cdot\text{CH}_2\text{CO}_2^-$ and $\text{HN}\cdot\text{CH}_2\text{CO}_2^-$ with yields of 63% and 37%, respectively. The amino radical cation, $^+\text{H}_2\text{N}\cdot\text{CH}_2\text{CO}_2^-$, suffers fast (≤ 100 ns) fragmentation into $\text{CO}_2 + \cdot\text{CH}_2\text{NH}_2$. The other primary radical, $\text{HN}\cdot\text{CH}_2\text{CO}_2^-$, can also be converted into the decarboxylating $^+\text{H}_2\text{N}\cdot\text{CH}_2\text{CO}_2^-$ by reaction with proton donors such as phosphate ($\text{H}_2\text{PO}_4^-/k = 7.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, and $\text{HPO}_4^{2-}/k = 2.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$) or the glycine zwitterion, Gly^\pm ($k = 3.9 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$), but only on a much longer (typically μs to ms) time scale ($k \approx 4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$). Competitively, the $\text{HN}\cdot\text{CH}_2\text{CO}_2^-$ transforms into a carbon-centered radical $\text{H}_2\text{N}\cdot\text{C}\cdot\text{H}\text{CO}_2^-$ either by an intramolecular 1,2-H-atom shift ($k = (1.2 \pm 1.0) \times 10^3 \text{ s}^{-1}$) or by bimolecular reaction with Gly^- ($k = (3.0 \pm 0.2) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$). Both C-centered radicals, $\text{H}_2\text{N}\cdot\text{C}\cdot\text{H}\text{CO}_2^-$ and $\cdot\text{CH}_2\text{NH}_2$, are reductants as verified through their reactions with $\text{Fe}(\text{CN})_6^{3-}$ and methyl viologen (MV^{2+}) in pulse-radiolysis experiments ($k \approx 4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$). The eventual complete transformation of all primary radicals into $\text{H}_2\text{N}\cdot\text{C}\cdot\text{H}\text{CO}_2^-$ and $\cdot\text{CH}_2\text{NH}_2$ was further substantiated by γ -radiolytic reduction of $\text{Fe}(\text{CN})_6^{3-}$. In the presence of suitable electron donors, the $\text{HN}\cdot\text{CH}_2\text{CO}_2^-$ radical acts as an oxidant. This was demonstrated through its reaction with hydroquinone ($k = (7.4 \pm 0.5) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$). Although the C-centered $\text{H}_2\text{N}\cdot\text{C}\cdot\text{H}\text{CO}_2^-$ radical is not generated in a direct H-atom abstraction by $\cdot\text{OH}$, this radical appears to be the exclusive product in the reaction of Gly^- with $(\text{CH}_3)_2\text{C}\cdot\text{OH}$, $\cdot\text{CH}_2\text{NH}_2$, and $\cdot\text{CH}_3$ ($k \approx 10^2 \text{ M}^{-1} \text{ s}^{-1}$). A most significant finding is that $\text{H}_2\text{N}\cdot\text{C}\cdot\text{H}\text{CO}_2^-$ can be converted into the decarboxylating N-centered radical cation $^+\text{H}_2\text{N}\cdot\text{CH}_2\text{CO}_2^-$ by reaction with proton donors such as Gly^\pm ($k \approx 3 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$) or phosphate and thus also becomes a source of CO_2 . The $\cdot\text{CH}_2\text{NH}_2$ -induced route establishes, in fact, a chain mechanism which could be proven through dose rate effect experiments and suppression of the chain upon addition of $\text{Fe}(\text{CN})_6^{3-}$ or MV^{2+} as a scavenger for the reducing precursor radicals. The possible initiation of amino acid decarboxylation by C-centered radicals and the assistance of proton donors at various stages within the overall mechanism are considered to be of general significance and interest in chemical and biological systems.

Introduction

The decarboxylation of carboxylic acids is an important reaction in chemistry and biochemistry. In its simplest form it can occur as a result of electron transfer from the carboxylate group at an electrode.¹ However, in amino acids it frequently also takes place as a secondary process, following electron removal from a neighboring amino,² thiomethoxy,^{3,4} or aromatic group.^{5,6} Those processes can be effected by photoexcited molecules or by free radical precursors, and in this regard,

glycine has received a great deal of attention. It serves as a model not only for the more complex amino acids but also for the amino polycarboxylic acids, such as nitritotriacetic acid and ethylenediaminetetraacetic acid (EDTA). These compounds are frequently used as complexing agents in inorganic chemistry and as such may be components in low-level nuclear waste. They have also found wide usage as sacrificial electron donors, for example, in photoreductions of porphyrins,⁷ flavins, and flavoenzymes,^{8,9} and in experimental studies of solar energy conversion.¹⁰

Evidence for the decarboxylation of glycine, following free radical attack, came from early studies of the X-ray and

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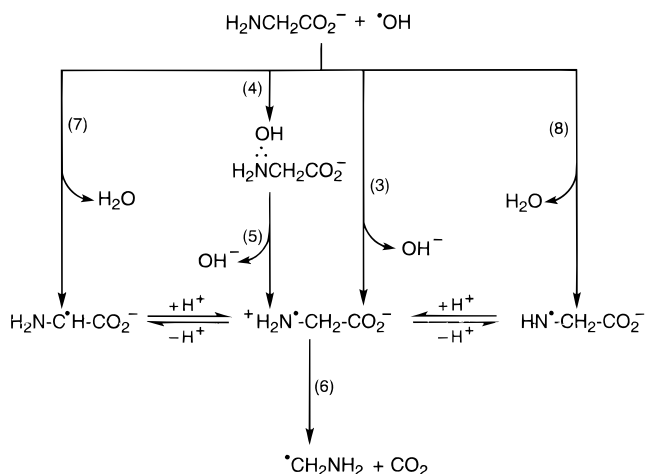
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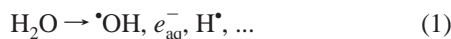
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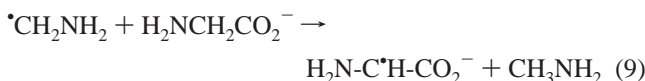
Scheme 1



γ -radiolysis of glycine solutions.^{11,12} Subsequently Mönig, Chapman, and Asmus² examined the effect of pH on CO₂ production from glycine and several other amino acids, which were subjected to reaction with •OH radicals. The latter were produced in γ -irradiated N₂O-saturated solutions, where the following reactions give rise to •OH and H•, accounting for about 90% and 10%, respectively, of reactive primary species available for further reaction.



It was found that above pH 6 the CO₂ yield rose and, depending on the structure of the amino acid, could be as high as the total yield of •OH radicals. Mönig et al. proposed formation of the CO₂ via reactions 3 or 4 plus 5, followed by 6 (see Scheme 1). The evidence for 6 came from the observation that reducing radicals were formed in a yield equal to that of the CO₂, which for glycine represented 65% of the total radical yield. The authors used halothane to detect the reducing species that they assigned to the α -amino radicals resulting from decarboxylation. The formation of reducing radicals from amino acids had also been observed in independent studies where various other scavengers were employed.^{13–15} However, in most of those studies, CO₂ was not determined, and the reduction was usually attributed to the H₂N-C•H-CO₂⁻ radical produced in reaction 7. At the time of those publications, this was the only radical identified by ESR in neutral or alkaline solutions of glycine, there being no evidence for reactions 3 to 6 or 8 in Scheme 1 with this amino acid.^{16,17} As a means of explaining why •CH₂-NH₂, the co-product of CO₂ in reaction 6, had not been observed in these earlier studies, Mönig et al.² proposed that in alkaline solution reaction 9 was fast enough to remove •CH₂NH₂ and



prevent its detection by ESR.

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Recent studies discussed the structures, thermochemistry, and reactions of glycine radicals in some detail.^{18–20} In particular, the relative stabilities of the H₂N-C•H-CO₂⁻, ⁺H₂N•-CH₂-CO₂⁻, and HN•-CH₂-CO₂⁻ radicals were examined, and it was shown that reaction 9 was feasible on thermochemical grounds.¹⁹ However, the rate is unknown, and experimental evidence for it is still lacking. A second point is that, although reducing radicals have been identified by pulse-radiolysis experiments, on the microsecond time scale they only accounted for ~60% of the total radicals present. The purpose of the present study was two-fold. First, to utilize a variety of scavengers in a pulse-radiolysis investigation, so that oxidizing radicals, such as the nitrogen-centered HN•-CH₂-CO₂⁻, might be detected, as well as the reducing C-centered species H₂N-C•H-CO₂⁻ and •CH₂-NH₂. Second, to examine the dependence of the CO₂ yield on the pH and glycine concentration in γ -radiolysis experiments in greater detail and to obtain evidence relating to reaction 9.

During the current work, it was found that •OH reacts about 500 times faster with the glycine anion than with the zwitterion (pK_a = 9.6).²¹ This is in agreement with earlier work.²² It also means that even at neutral pH, •OH preferentially attacks the anion. Thus, it was decided that the present paper should concentrate on radicals produced by that process in experiments where the basic form of glycine, Gly⁻, prevails, that is, in basic solutions. Reactions induced by •OH attack on the zwitterion will be reported elsewhere. The system of glycine radicals turned out to be surprisingly complex. For example, it was found that carbon-centered radicals could initiate CO₂ formation from glycine anion, though not as well as •OH. Furthermore, concrete evidence was found that acid–base reactions are able to convert both the oxidizing HN•-CH₂-CO₂⁻ and the reducing H₂N-C•H-CO₂⁻ radicals into the decarboxylating ⁺H₂N•-CH₂-CO₂⁻ radical. The end result is that CO₂ can be formed via a chain reaction, albeit with a somewhat short chain length.

Experimental Section

Materials. Chemicals were purchased from Aldrich, Fluka, or Sigma. All were of reagent grade or better and were used without further purification. Solutions were prepared with Millipore Milli-Q purified water. The pH of the solutions was adjusted with NaOH. All manipulations with solutions used for the CO₂ determinations were done under a N₂ atmosphere. All solutions were saturated with N₂O before irradiation.

Pulse-Radiolysis. Pulse-radiolysis experiments were carried out using the Notre Dame 8-MeV Titan Beta model TBS-8/16-1S linear accelerator with a pulse length of 2.5 ns. Absorbed doses were on the order of 2–8 Gy (J kg⁻¹) per pulse. Dosimetry was carried out with N₂O-saturated solutions of 10 mM KSCN assuming $\epsilon_{472\text{nm}}((\text{SCN})_2^{\bullet-}) = 7580 \text{ M}^{-1} \text{ cm}^{-1}$ and $G = 6.13$, where G denotes the number of species formed per 100 eV of absorbed energy ($G = 1$ corresponds to 0.1036 $\mu\text{M J}^{-1}$ in SI units). A basic description of the pulse-radiolysis setup, data collection system, and details of dosimetry have been reported elsewhere.^{23,24} The data-acquisition subsystem has been upgraded to include a Spex 270M monochromator, a LeCroy 7200A digital storage oscilloscope, and a PC-AT compatible computer. Experiments were performed with continuously flowing solutions.

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Table 1. Yields of Bleached $\text{Fe}(\text{CN})_6^{3-}$ Expressed as Absolute G Values, $G(-\text{Fe}(\text{CN})_6^{3-})$, and $G(\cdot\text{OH}) + G(\text{H}\cdot)$ as a Function of (a) $[\text{Fe}(\text{CN})_6^{3-}]$, (b) [glycine], and (c) pH^a

[Gly] (M)	$[\text{Fe}(\text{CN})_6^{3-}]$ (mM)	dose rate (Gy min ⁻¹)	pH	$G(-\text{Fe}(\text{CN})_6^{3-})$	$G(\cdot\text{OH}) + G(\text{H}\cdot)$
(a)					
0.1	0.2	19	10.6	7.1	7.3
0.1	0.5	19	10.6	7.3	7.3
0.1	1.0	19	10.6	7.3	7.3
(b)					
0.001	0.5	6	10.6	5.5	6.1
0.01	0.5	6	10.6	6.5	6.5
0.01	0.5	19	10.6	5.9	6.5
0.1	0.5	60	10.6	7.3	7.3
1	0.5	19	10.6	8.1	8.1
(c)					
0.1	0.5	6	11.0	7.5	7.3
0.1	0.5	19	10.6	7.3	7.3
0.1	0.5	19	9.6	7.2	7.1
0.1	0.5	6	9.0	6.8	6.8

^a Steady-state, γ -radiolysis measurements in N_2O -saturated aqueous solutions. Standard deviations ± 0.1 or less.

Analysis of optical absorption vs time traces was carried out using ORIGIN (Microcal). Both absorption intensities and kinetic data were corrected for long-term decays due to radical-radical reactions or other processes.

γ -Radiolysis. γ -Irradiation of samples was carried out in the field of ⁶⁰Co sources at dose rates in the range of 2–60 Gy min⁻¹. Absorbed doses in the irradiated samples were determined by Fricke dosimetry.

CO_2 Determination. Concentrations of CO_2 (as HCO_3^-) were quantitatively determined by means of high-performance ion chromatography (Dionex 2010i, Ion Pac ICE-AS1 column) as previously described.²⁵ Prior to analysis, solutions were treated by appropriate dilution and addition of NaOH stock solution to achieve an ionic strength ≤ 0.1 M and pH ~ 12 . $G(\text{CO}_2)$ values were calculated from linear concentration vs dose plots for at least 3 different doses.

$\text{Fe}(\text{CN})_6^{3-}$ Consumption. Quantitative determinations of $\text{Fe}(\text{CN})_6^{3-}$ concentration after γ -irradiation were made by measuring the 420-nm absorbance on a Milton Roy Spectronic 3000 spectrophotometer with ϵ taken as 1020 M⁻¹ cm⁻¹.²⁶ $G(-\text{Fe}(\text{CN})_6^{3-})$ values were calculated from linear concentration vs dose plots for at least 3 different doses.

Experimental Parameters. The yields of $\cdot\text{OH}$ radicals available for reaction with substrates in N_2O -saturated solutions were calculated according to the formula²⁶

$$G(\cdot\text{OH}) = 5.2 + 3.0 \frac{\sqrt{k_s[\text{S}]/4.7 \times 10^8}}{1 + \sqrt{k_s[\text{S}]/4.7 \times 10^8}} \quad (\text{I})$$

where [S] and k_s denote the concentration of a substrate S and the rate constant of its reaction with hydroxyl radicals, respectively. For the yield of H-atoms formed in the radiolysis of water, a value $G(\text{H}\cdot) = 0.6$ was used. Total yields of radicals reacting with glycine were taken to be $\{G(\cdot\text{OH}) + G(\text{H}\cdot)\}$.

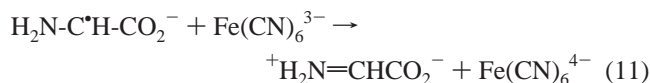
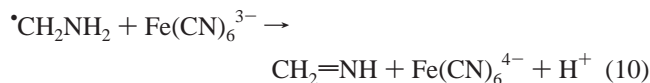
All experiments were done at room temperature (~ 23 °C). Experimental error limits are estimated to be $\pm 10\%$ unless specifically noted.

Results

Total Glycine Radical Yields and $G(-\text{Fe}(\text{CN})_6^{3-})$. Both in pulse- and γ -radiolysis, $G(\cdot\text{OH})$, the yield of $\cdot\text{OH}$ radicals actually scavenged by glycine, changes with [Gly] in accord with expression I, and it is necessary to take account of this in comparing yields of oxidizing or reducing radicals and stable products formed under different conditions. In using expression I, allowance must be made for the change in the proportions of

the $^+\text{H}_3\text{NCH}_2\text{CO}_2^-$ zwitterionic form, (Gly^\pm) , and the $\text{H}_2\text{NCH}_2\text{CO}_2^-$ anion form, (Gly^-) , with pH since the two have very different rate constants for reaction with $\cdot\text{OH}$, namely 1×10^7 and 5.3×10^9 M⁻¹ s⁻¹, respectively.^{21,22} Values of $\{G(\cdot\text{OH}) + G(\text{H}\cdot)\}$ calculated for several concentrations of glycine and pHs are shown in Table 1.

Also shown in Table 1 are values of $G(-\text{Fe}(\text{CN})_6^{3-})$ from γ -radiolysis experiments. A very important point is that the $G(-\text{Fe}(\text{CN})_6^{3-})$ and $\{G(\cdot\text{OH}) + G(\text{H}\cdot)\}$ are equal within the experimental uncertainty of ± 0.1 G unit, except for some relatively low concentrations of glycine or $\text{Fe}(\text{CN})_6^{3-}$ where $\cdot\text{OH}$ and $\text{H}\cdot$ may engage in some initial combination reactions. That feature means that all radicals produced by $\cdot\text{OH}$ or $\text{H}\cdot$ attack on glycine in γ -radiolysis are capable of reducing $\text{Fe}(\text{CN})_6^{3-}$. This, in turn, suggests that initially nonreducing species are converted to either $\cdot\text{CH}_2\text{NH}_2$ or $\text{H}_2\text{N}\cdot\text{C}\cdot\text{H}\text{-CO}_2^-$ so that reactions



10 and 11 can occur. In earlier work, a full yield of reducing radicals was also found for the case of flavin reductions in γ -irradiated glycine solutions.¹⁵ One important purpose of the pulse studies described below was to determine how this happened.

It should be noted that for the conditions of pH and glycine concentration in Table 1, the change in absorbance was proportional to the absorbed dose down to the complete disappearance of $\text{Fe}(\text{CN})_6^{3-}$, which was quantitatively converted into $\text{Fe}(\text{CN})_6^{4-}$ as confirmed by measurements of its characteristic optical spectrum. Only at lower pHs the rate of reduction of $\text{Fe}(\text{CN})_6^{3-}$ fell off with dose. This can be attributed to a direct reaction of $\cdot\text{OH}$ radicals with the $\text{Fe}(\text{CN})_6^{4-}$ that accumulated in the solution, so that reoxidation to $\text{Fe}(\text{CN})_6^{3-}$ became increasingly probable at longer irradiation times. The difference from higher pH values was due to the increase in the $[\text{Gly}^\pm]/[\text{Gly}^-]$ ratio in conjunction with the low rate constant for the reaction of $\cdot\text{OH}$ radicals with Gly^\pm . Table 1, therefore, only contains the results for the solutions where a reliable estimate of the initial slope of the ΔOD vs dose plot was possible.

The agreement between $G(-\text{Fe}(\text{CN})_6^{3-})$ and $\{G(\cdot\text{OH}) + G(\text{H}\cdot)\}$ means that the latter quantity, calculated as described above for given conditions, actually does reflect the total yield of glycine radicals formed in γ -radiolysis. As a means of compensating for changes in the number of glycine radicals produced at different pHs and concentrations, in the remainder of this paper, yields of radicals and CO_2 are reported relative to the total of $\{G(\cdot\text{OH}) + G(\text{H}\cdot)\}$. For example, the relative yield of CO_2 under a specified set of conditions would be $G_{\text{rel}}(\text{CO}_2) = G(\text{CO}_2)/\{G(\cdot\text{OH}) + G(\text{H}\cdot)\}$. Tables with absolute yields and values of $\{G(\cdot\text{OH}) + G(\text{H}\cdot)\}$ have been submitted as Supporting Information.

Measurements of Radical Reactions by Pulse Radiolysis. Reducing Radicals. In the current study, not only $\text{Fe}(\text{CN})_6^{3-}$ but also methyl viologen (MV^{2+}) were used to scavenge reducing radicals, and the respective kinetics were observed in real time by means of pulse radiolysis. Conversion of MV^{2+} into the radical cation $\text{MV}^{\cdot+}$ was followed spectrophotometrically at 600 nm. The extinction coefficient ($\epsilon = 12\,820$ M⁻¹

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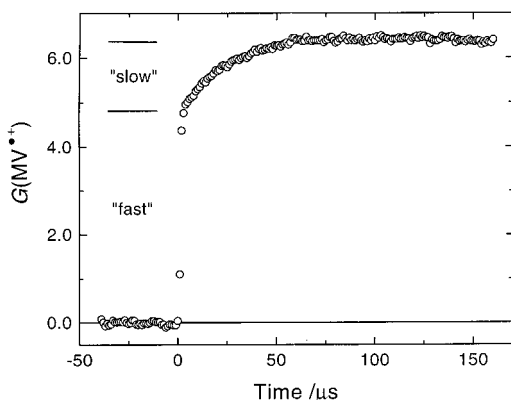


Figure 1. Yield of $MV^{\bullet+}$, calculated from the optical absorption at 600 nm, as a function of time in a pulse-irradiated, N_2O -saturated aqueous solution containing 1 M glycine and 1.2 mM MV^{2+} at pH 11.0.

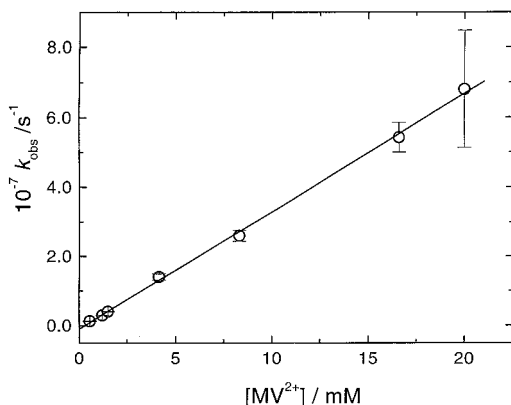
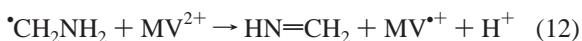


Figure 2. Plot of k_{obs} for the fast $MV^{\bullet+}$ formation versus MV^{2+} concentration measured at 600 nm in pulse-irradiated, N_2O -saturated aqueous solution containing 1 M glycine and MV^{2+} at pH 11.0.

cm^{-1} , based on $G = 7.14$ as calculated by eq I) was measured in a separate set of experiments by using $CO_2^{\bullet-}$ generated in N_2O -saturated 0.1 M formate solutions as the reductant. It is within the range of published values.

Figure 1 shows the trace of an optical absorption measured at 600 nm as a function of time in a pulse-irradiated N_2O -saturated solution containing 1 M glycine and 1.2 mM methyl viologen at pH 11. Two kinetically distinguishable processes of $MV^{\bullet+}$ formation can be clearly seen; about $2/3$ of the trace intensity was developed very fast, within a few μs after the electron pulse, and about $1/3$ via a considerably slower process ($t_{1/2} \approx 15 \mu s$). Variation of the MV^{2+} concentration (0.5–20 mM) in the same solution influenced only the rate of the fast process, whereas the slow process was not changed at all by this parameter. The latter can be assumed to be associated with the reactions that convert nonreducing species into reducing radicals on the γ -radiolysis time scale.

The fast formation process (analyzed on an appropriately expanded time scale and avoiding experimental points within the pulse duration of ca. 10 ns) was pseudo-first-order, namely, k_{obs} was linearly proportional to $[MV^{2+}]$ as shown in Figure 2. From the slope of the straight line, the second-order rate constant for the MV^{2+} reduction of $(3.3 \pm 0.2) \times 10^9 M^{-1} s^{-1}$ was calculated. For reasons explained below, this can be associated exclusively with reaction 12. It is similar to values obtained



for the reduction of methyl viologen by other α -amino radicals

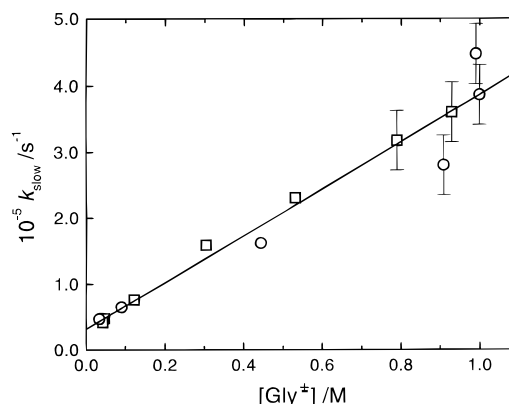


Figure 3. Plot of k_{slow} for $MV^{\bullet+}$ formation (O) and $Fe(CN)_6^{3-}$ bleaching (□) versus $[Gly^{\pm}]$ measured at 600 and 420 nm, respectively, in pulse-irradiated, N_2O -saturated aqueous solutions containing 1 M glycine and 0.5 mM MV^{2+} or 1 mM $Fe(CN)_6^{3-}$ at different pHs in the range of 8.6–11.

such as $H_2N-C^{\bullet}H-CO_2Et$ ²¹ and the α -aminoalkyl radical $CH_3-SCH_2CH_2-C^{\bullet}H-NH_2$ formed after decarboxylation of the one-electron oxidized methionine.^{3,27}

Very similar results were obtained when $Fe(CN)_6^{3-}$ was used as the scavenger of reducing radicals. In such systems, the bleaching of the $Fe(CN)_6^{3-}$ chromophore at 420 nm ($\epsilon = 1020 M^{-1} cm^{-1}$) was followed. The bleaching occurred in two steps with similar kinetics and yield ratio to those observed for the MV^{2+} reduction. The kinetics of the slow process was again independent of the scavenger concentration.

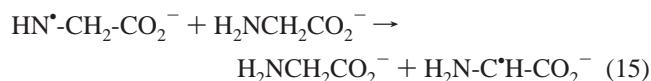
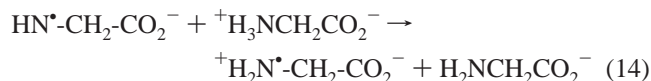
Both for MV^{2+} and $Fe(CN)_6^{3-}$, the kinetics of the slow part of the reduction exhibited a strong dependence on pH and, most importantly, also on the glycine concentration. A quantitative evaluation of the kinetics was done for a system of 1 M glycine with both 0.5 mM MV^{2+} and 1 mM $Fe(CN)_6^{3-}$ at different pH values between 8 and 11. The slow formation kinetics was always exponential, but the formation accelerated as the pH of the solution decreased. Since the change of pH in this region causes only a change in the ratio of the anionic (Gly^-) vs the zwitterionic form (Gly^{\pm}) of glycine, the first-order rate constants for the slow formation kinetics, k_{slow} , were plotted against the actual Gly^{\pm} concentration calculated for the various pHs at which experiments were conducted by using $pK_{13} = 9.6$. The



results are shown in Figure 3. There is indeed a good correlation with a linear plot, but there is a pronounced intercept indicating an additional reaction (or reactions) forming radicals, which reduce MV^{2+} .

The only possible group of radicals not capable of reducing MV^{2+} and other electron acceptors directly are the initially oxidizing N-centered radicals, namely, $^+H_2N^{\bullet}-CH_2-CO_2^-$ and $HN^{\bullet}-CH_2-CO_2^-$. Evidence to be presented later indicates that the $^+H_2N^{\bullet}-CH_2-CO_2^-$ radical is too short lived ($\tau \leq 10^{-7} s$) to account for any slow secondary and glycine-concentration-dependent process. Thus, $HN^{\bullet}-CH-CO_2^-$ is the only plausible species to be involved in conversions to the reducing $^{\bullet}CH_2NH_2$ and/or $H_2N-C^{\bullet}H-CO_2^-$ radicals under the conditions for Figure

3. This may be rationalized in terms of the following possible reactions



In 14 the glycine zwitterion acts as a proton donor, while in 14a the proton comes from H₂O. Both will be followed immediately by the decarboxylation reaction 6. Reaction 15, a competing process with the anionic form of Gly, is an H-atom abstraction, and reaction 16 is an intramolecular 1,2-H atom shift. Both are exothermic¹⁹ and thus feasible. The expression for the overall rate constant of the slow process of the MV^{•+} formation would then be

$$k_{\text{slow}} = k_{14}[\text{Gly}^{\pm}] + k_{15}[\text{Gly}^-] + k_a \quad (\text{II})$$

where k_a is $\{k_{14a}[\text{H}_2\text{O}] + k_{16}\}$. Introducing

$$[\text{Gly}]_{\text{total}} = [\text{Gly}^{\pm}] + [\text{Gly}^-] \quad (\text{III})$$

into equation II gives expression IV

$$k_{\text{slow}} = (k_{14} - k_{15})[\text{Gly}^{\pm}] + k_{15}[\text{Gly}]_{\text{total}} + k_a \quad (\text{IV})$$

Analysis of the data in Figure 3 in terms of this expression yields $(k_{14} - k_{15}) = (3.5 \pm 0.2) \times 10^5 \text{ s}^{-1}$ and $\{k_{15} \times 1.0 + k_a\} = (3.1 \times 0.2) \times 10^4 \text{ s}^{-1}$ from the slope and intercept, respectively.

Further analysis was done by following the rate of the slow Fe(CN)₆³⁻ bleach in N₂O-saturated, pH 10.6, solutions containing 5, 50, and 100 mM glycine and with [Fe(CN)₆³⁻] = 0.5 or 1 mM. For those conditions, the first-order rate constant k_{slow} was found to be 1.5×10^3 , 3.8×10^3 , and $8.0 \times 10^3 \text{ s}^{-1}$, respectively. From these results and the values of $(k_{14} - k_{15})$ and $\{k_{15} + k_a\}$ derived from the 1 M glycine data above, one finds by solving simultaneous equations $k_{14} = (3.9 \pm 0.3) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, $k_{15} = (3.0 \pm 0.2) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, and $k_a = \{k_{14a} \times [\text{H}_2\text{O}] + k_{16}\} = (1.2 \pm 1.0) \times 10^3 \text{ s}^{-1}$. Little can be said about the possible contribution of $k_{14a} \times [\text{H}_2\text{O}]$ (reaction 14a has been included primarily for completeness). The percentage error on k_a is relatively large because of the difficulty of properly correcting for second-order decays in the traces. However, it may be noted that the above parameters also gave consistent results in the analysis of the data for the scavenging of oxidizing radicals. In summary k_{slow} was given by

$$k_{\text{slow}} = (3.9 \pm 0.3) \times 10^5 [\text{Gly}^{\pm}] + (3.0 \pm 0.2) \times 10^4 \times [\text{Gly}^-] + (1.2 \pm 1.0) \times 10^3 \text{ s}^{-1} \quad (\text{V})$$

There was one significant difference between the results with Fe(CN)₆³⁻ and MV²⁺, which occurred in systems with low glycine concentration, i.e., having small values of k_{slow} . While

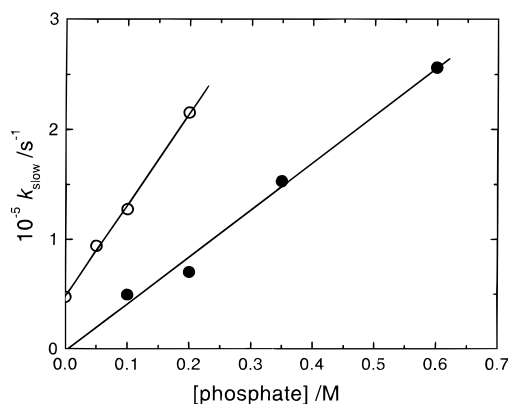


Figure 4. Plot of k_{slow} for MV^{•+} formation versus total phosphate buffer concentration measured at 600 nm in pulse-irradiated, N₂O-saturated aqueous solution containing 0.1 M glycine, 0.5 mM MV²⁺, and phosphate at pH 9.8 (●) and pH 9.3 (○).

the optical absorption traces for Fe(CN)₆³⁻ did not show any decay (i.e., re-oxidation of Fe(CN)₆⁴⁻) up to the longest time scale (2 ms) used, the MV^{•+} absorptions, in contrast, exhibited a dose-dependent (i.e., second-order) decay on a ms time scale of up to ca. half of the maximum intensity. Since MV^{•+} is a stable radical in the absence of molecular oxygen, a reasonable explanation for that would be reoxidation to MV²⁺ by the HN[•]-CH₂-CO₂⁻, H⁺/H₂NCH₂CO₂⁻ has been estimated to be 1.7 V,¹⁹ and $E(\text{HN}^{\bullet}\text{-CH}_2\text{-CO}_2^-, \text{H}^+/\text{H}_2\text{NCH}_2\text{CO}_2^-)$ in the region of pH 10 would thus be ~1.1 V. Given $E^0(\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}) = +0.358 \text{ V}$ and $E^0(\text{MV}^{2+}/\text{MV}^{\bullet+}) = -0.448 \text{ V}$,²⁸ at pH 10 the difference in reduction potentials for (HN[•]-CH₂-CO₂⁻, H⁺/H₂NCH₂CO₂⁻) and (MV²⁺/MV^{•+}) (~1.6 V) would be much larger than that for (HN[•]-CH₂-CO₂⁻, H⁺/H₂NCH₂CO₂⁻) and (Fe(CN)₆³⁻/Fe(CN)₆⁴⁻) (~0.7 V). Thus, one would expect HN[•]-CH₂-CO₂⁻-induced oxidation of Fe(CN)₆⁴⁻ to be much slower than that of MV^{•+}. This was confirmed independently in an experiment where 1 mM Fe(CN)₆⁴⁻ was added to a N₂O-saturated solution of 0.1 M glycine at pH 11. No formation of Fe(CN)₆³⁻ absorption at 420 nm was observed in the time up to 2 ms after the electron pulse.

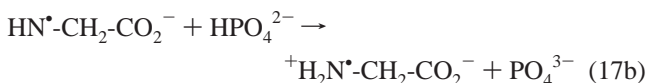
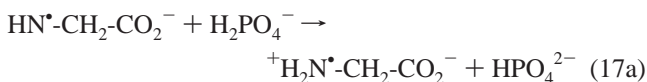
Gly[±] in reaction 14 is assumed to act as a proton donor, and it was of interest to determine whether other proton donors could also effect the N-protonation of HN[•]-CH₂-CO₂⁻. At 0.1 M glycine, there was practically no slow formation of MV^{•+} detectable, but after addition of only 0.1 M phosphate, the slow formation of MV^{•+} reappeared giving a total MV^{•+} yield equal to $\{G(\bullet\text{OH}) + G(\text{H}^{\bullet})\}$. Furthermore, the slow formation kinetics was exponential, and the pseudo-first-order rate constant changed proportionally to the phosphate concentration, as shown in Figure 4 (N₂O-saturated, 0.1 M glycine, 0.5 mM MV²⁺, pH 9.8). An analogous experiment was performed at pH 9.3. At both pHs, straight lines were obtained, yielding apparent second-order rate constants of $8.2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ (pH 9.3) and $4.3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ (pH 9.8), respectively. This pH dependence suggests not only that proton donation occurs from HPO₄²⁻, the prevalent form of phosphate at these pHs, but also that the small concentration of its conjugate acid, H₂PO₄⁻, significantly contributes. On the basis of $\text{p}K_a = 7.2$ for the H₂PO₄⁻ ⇌ HPO₄²⁻ + H⁺ equilibrium, bimolecular rate constants of $k_{17a} = 7.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{17b} = 2.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ have been

Table 2. Relative Yields of CO₂ from γ -Radiolysis and Reducing and Oxidizing Radicals from Pulse-Radiolysis

radical scavengers	$G_{\text{rel}}(\text{CO}_2)$	$G_{\text{rel}}(\text{reducing})$	$G_{\text{rel}}(\text{oxidizing})$	$G_{\text{rel}}(\text{total})$
<i>pulse</i>				
MV ²⁺		0.59 ± 0.04 ^a	0.31 ± 0.05 ^a	0.90 ^a
Fe(CN) ₆ ³⁻		0.46 ± 0.04 ^a	0.36 ± 0.05 ^a	0.82 ^a
HQ ⁻			0.34 ± 0.04 ^b	
γ				
MV ²⁺	0.58 ^c			
Fe(CN) ₆ ³⁻	0.58 ^c			1.00 ^a
no scavenger, 1 and 5 mM Gly	0.70			

^a Average over several experiments. ^b From extrapolation to infinite [scavenger] based on expression VII. ^c Plateau yields.

evaluated from our experimental data for the respective underlying reactions



17a and 17b. This result strongly supports the interpretation that the role of Gly[±] in that reaction is indeed also that of a proton donor.

The yields of reduction observed on the fast and slow time scales, relative to $\{G(\bullet\text{OH}) + G(\text{H}^{\bullet})\}$, were tabulated for both MV²⁺ and Fe(CN)₆³⁻ for a variety of conditions and are available as Supporting Information. Except for the slow part of MV²⁺ reduction in the absence of phosphate, they did not exhibit any significant dependence on pH from 8 to 11 or on [Gly] from 0.1 to 1 M. Average values for those conditions have been presented in Table 2 under the headings G_{rel} (reducing) and G_{rel} (oxidizing) since they are considered to be associated with $\{\text{H}_2\text{N-C}^{\bullet}\text{H-CO}_2^- + \bullet\text{CH}_2\text{NH}_2\}$ and $\text{HN}^{\bullet}\text{-CH}_2\text{-CO}_2^-$, respectively.

Oxidizing Radicals. To obtain direct evidence for the formation of oxidizing radicals as a result of the Gly⁻ reaction with $\bullet\text{OH}/\text{H}^{\bullet}$ radicals at high pH, hydroquinone (HQ) was used as a scavenger. This compound was selected because of its low reduction potential ($E^0[\text{Q}^{\bullet-}/\text{Q}^{2-}] = 0.023 \text{ V}$).^{29,30} Also, by using hydroquinone, its one-electron oxidized product, semiquinone anion ($\text{Q}^{\bullet-}$), could be conveniently detected by means of optical absorption measurements ($\lambda_{\text{max}} = 427 \text{ nm}$, $\epsilon = 7200 \text{ M}^{-1} \text{ cm}^{-1}$).^{31,32} The semiquinone radical was indeed formed when N₂O-saturated solutions of glycine at pH 11 containing hydroquinone were pulse irradiated. The experimental traces were, however, not stable on the ms time scale but showed a dose-dependent, second-order decay. Similar to the explanation put forward for the decay of the methyl viologen radical cation, it is proposed that this decay, subsequent to the semiquinone formation, is due to its reduction back to hydroquinone by the glycine-derived reducing radicals that were simultaneously formed in the solution as described above. The pseudo-first-order rate constants for the semiquinone formation were, therefore, obtained by fitting the experimental data to an

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(31) Adams, G. E.; Michael, B. D. *Trans. Faraday Soc.* 1967, 63, 1171.

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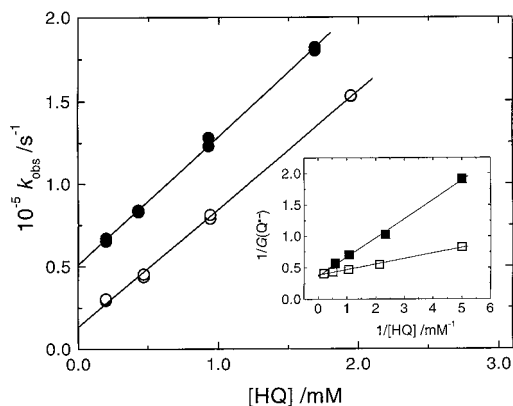
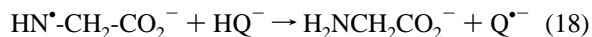


Figure 5. Plot of k_{obs} for semiquinone formation versus [HQ] measured at 427 nm in pulse-irradiated, N₂O-saturated aqueous solution at pH 11.0 containing hydroquinone and 0.1 M glycine (open symbols) or 1 M glycine (filled symbols). Inset: Plot of reciprocal semiquinone yield expressed as $G(\text{Q}^{\bullet-})$ versus $[\text{HQ}]^{-1}$ in the same solutions as in the main figure.

expression with a sequential growth and decay in the analysis with ORIGIN (Microcal). Results are shown in Figure 5 as k_{obs} versus hydroquinone concentration for two systems containing 0.1 and 1 M glycine, respectively, at pH 11. Good linear fits are obtained with identical slopes, which are interpreted as the rate constant for reaction 18.



At this pH hydroquinone is present mainly in the HQ⁻ form. The three different protonation forms, i.e., H₂Q, HQ⁻, and Q²⁻, are in the ratio of 6:72:23, respectively ($\text{p}K_1 = 10.35$; $\text{p}K_2 = 11.5$).²⁹ The result, $k_{18} = (7.4 \pm 0.5) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, is therefore a weighted value for this composition.

For each HQ concentration, the straight line in Figure 5 does not go through the origin but shows an intercept, which is larger for the higher glycine concentration. This is because reaction 18 is in competition with the processes considered above as contributing to k_{slow} . The total rate of removal of $\text{HN}^{\bullet}\text{-CH}_2\text{-CO}_2^-$ is in fact $\{k_{18}[\text{HQ}] + k_{\text{slow}}\}$. For each [Gly] in Figure 5, k_{slow} should, therefore, correspond to the intercept. Numerically, the intercepts amount to 1.5×10^4 and $5.1 \times 10^4 \text{ s}^{-1}$ for the 0.1 and 1 M glycine systems, respectively. The k_{slow} values calculated from expression IV, $0.6 \times 10^4 \text{ s}^{-1}$ and $4.5 \times 10^4 \text{ s}^{-1}$, respectively, are in acceptable agreement.

The yield of semiquinone radicals was calculated from the measured absorbances by using the known $\text{Q}^{\bullet-}$ extinction coefficient. The competition between reaction 18 and the k_{slow} processes causes this yield to increase with the concentration of hydroquinone in accord with expression VI, in which $G(\text{Q}^{\bullet-})$

$$\frac{G(\text{Q}^{\bullet-})}{G(\text{HN}^{\bullet-})} = \frac{k_{18}[\text{HQ}]}{k_{18}[\text{HQ}] + k_{\text{slow}}} \quad (VI)$$

is the semiquinone radical yield and $G(\text{HN}^{\bullet-})$ that of the oxidizing $\text{HN}^{\bullet}\text{-CH}_2\text{-CO}_2^-$ radicals. Re-arrangement gives

$$\frac{1}{G(\text{Q}^{\bullet-})} = \frac{1}{G(\text{HN}^{\bullet-})} \left(1 + \frac{k_{\text{slow}}}{k_{18}[\text{HQ}]} \right) \quad (VII)$$

Plots of the reciprocal semiquinone radical yield versus reciprocal hydroquinone concentration for both 0.1 and 1 M glycine are shown in the inset of Figure 5. From the intercepts of the straight lines, $G(\text{Q}^{\bullet-}) = 2.7$ and 2.5 are obtained, respectively,

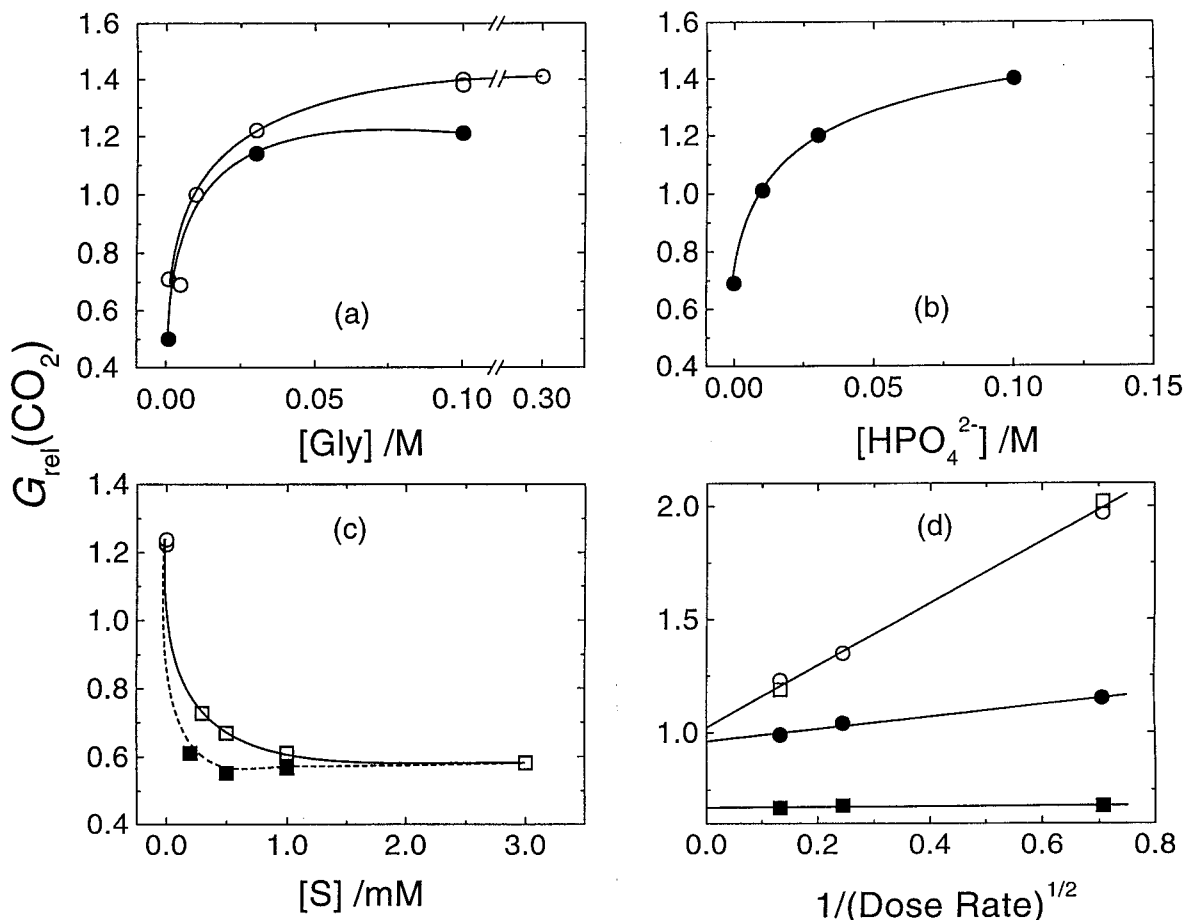


Figure 6. $G_{\text{rel}}(\text{CO}_2)$ obtained after γ -radiolysis of N_2O -saturated aqueous solutions versus (a) glycine concentration at a dose rate of 60 Gy min^{-1} , pH 10.6 (O) and pH 7.6 (●). (b) Concentration of phosphate buffer at 0.005 M Gly and pH 10.6, dose rate of 60 Gy min^{-1} . (c) Concentration of scavengers of reducing radicals MV^{2+} (■) and $\text{Fe}(\text{CN})_6^{3-}$ (□) at 0.03 M Gly, pH 10.6, dose rate of 60 Gy min^{-1} (O, same system with no scavenger). (d) Reciprocal square root of dose rate (in Gy min^{-1}) for N_2O -saturated aqueous solutions containing 0.005 M Gly (■), 0.01 M Gly (●), 0.03 M Gly (O), 0.005 M Gly and 0.03 M Na_2HPO_4 (□) at pH 10.6.

at infinite hydroquinone concentration. These amount to relative yields of 0.37 and 0.31, if expressed as fractions of $\{G(\cdot\text{OH}) + G(\text{H}\cdot)\}$ for the 0.1 and 1.0 M solutions. The average of 0.34 ± 0.04 is given in column four of Table 2. The agreement with the $\text{Fe}(\text{CN})_6^{3-}$ and MV^{2+} values for $G_{\text{rel}}(\text{oxidizing})$ supports the conclusion that the slow process is due to the conversion of the $\text{HN}\cdot\text{CH}_2\text{CO}_2^-$ oxidizing radical to reducing species.

CO_2 Yields from γ -Radiolysis Experiments. Effect of Proton Donors. The yields of CO_2 following γ -radiolysis of N_2O -saturated 1 and 5 mM glycine solutions at pH 10.6, were $G = 4.30$ and 4.35 , respectively, in good agreement with $G = 4.0$ obtained earlier for 5 mM glycine at pH 9–11.² When expressed as fractions of $\{G(\cdot\text{OH}) + G(\text{H}\cdot)\}$, the present results for these dilute solutions correspond to $G_{\text{rel}}(\text{CO}_2) = 0.70 \pm 0.02$. Values of $G_{\text{rel}}(\text{CO}_2)$ for a variety of other concentrations of glycine and pH, and with different dose rates and concentrations of phosphate and scavengers are shown in Figure 6a–d. The experimental CO_2 yields and yields of $\{G(\cdot\text{OH}) + G(\text{H}\cdot)\}$ from which the $G_{\text{rel}}(\text{CO}_2)$ data points were calculated are available in the Supporting Information part of this paper.

Figure 6a shows the effect of glycine concentration at pH 7.6 and 10.6 for a dose rate of 60 Gy min^{-1} . In both cases there is a steep rise in $G_{\text{rel}}(\text{CO}_2)$ over the 5 to 50 mM range, and then further increases are relatively small. Varying the pH between 6 and 11 at constant glycine concentration (0.03 M) had practically no influence on the CO_2 yields, which were all at the range of $G_{\text{rel}} = 1.1$ to 1.2. The 0.03 M data in Figure 6a illustrate that point for solutions at pH 7.6 and 10.6. The most

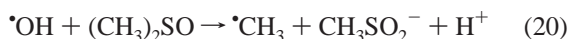
important feature of the results is that the yields of CO_2 increased to values significantly above $\{G(\cdot\text{OH}) + G(\text{H}\cdot)\}$ at high glycine concentration. This finding indicates the possibility of a chain reaction, though probably with a relatively short length. The occurrence of a chain reaction is confirmed by the inverse dependence of the yields on the square root of the dose rate in Figure 6d for pH 10.6. There, one can see that for 0.03 M glycine at the lowest dose rate (2 Gy min^{-1}) $G_{\text{rel}}(\text{CO}_2)$ actually rises to twice the yield of $\{G(\cdot\text{OH}) + G(\text{H}\cdot)\}$. The plots for all three of the concentrations are linear, and the slopes increase with $[\text{Gly}]$, which implies a rate-limiting step for the chain process involving either Gly^\pm , Gly^- , or both. The relatively large intercepts indicate a high proportion of nonchain CO_2 , and for 0.005 M Gly, this appears, in effect, to be the only significant process.

A most interesting feature in Figure 6d is the fact that the originally dose rate independent data for 0.005 M Gly coincide with the dose rate dependent points for 0.03 M Gly when 0.03 M phosphate is added. This implies that a proton source is important in the chain-propagating step and, in the absence of phosphate, Gly^\pm would fill that role. The ability of phosphate to replace Gly^\pm is reinforced by the general similarity in the dependencies of $G_{\text{rel}}(\text{CO}_2)$ on $[\text{Gly}]$ and $[\text{phosphate}]$ at pH 10.6 which can be seen from a comparison of Figure 6a and 6b to be virtually identical.

The presence of scavengers also influenced the yield of CO_2 , as can be appreciated from Figure 6c. MV^{2+} and $\text{Fe}(\text{CN})_6^{3-}$ suppressed $G_{\text{rel}}(\text{CO}_2)$ to the same limiting value of 0.58. This is

only slightly less than $G_{\text{rel}}(\text{CO}_2) = 0.70 \pm 0.02$ obtained in 0.001 and 0.005 M glycine, where the chain length is almost negligible. Since the pulse-radiolysis experiments in effect showed that MV^{2+} and $\text{Fe}(\text{CN})_6^{3-}$, while being unreactive to $\text{HN}^{\bullet}\text{-CH}_2\text{-CO}_2^-$, successfully reacted with $\text{CH}_2\text{NH}_2^{\bullet}$ and $\text{H}_2\text{N-C}^{\bullet}\text{H-CO}_2^-$, one can assume that it is primarily these reducing species that are the chain-carrying radicals. The first of them would be the precursor of the second in reaction 9.

Alkyl Radical Mediated Decarboxylation. Experiments were also performed with systems where all of the primary water radicals were fully converted into alkyl radicals *before they could react with glycine*. For this purpose, N_2O -saturated solutions containing 0.03 M glycine were irradiated in the presence of 1 M 2-propanol or dimethyl sulfoxide, which were added to scavenge OH^{\bullet} radicals and convert them quantitatively into $(\text{CH}_3)_2\text{C}^{\bullet}\text{OH}$ and CH_3^{\bullet} radicals, respectively (2-propanol also converts H^{\bullet} into $(\text{CH}_3)_2\text{C}^{\bullet}\text{OH}$), reactions 19 and 20. (For



mechanisms and respective rate constants see refs 22, 33, 34.) The resulting C-centered radicals (R^{\bullet}) could then, in principle, either undergo radical-radical termination reactions, which do not form CO_2 as a product or react with glycine anion via an H-atom abstraction from the CH_2 group. The C-H bonds at this site are relatively weak ($D_{\text{C-H}} = 363 \text{ kJ mol}^{-1}$) due to the combined stabilizing effects of the N lone-pair and the carboxyl,¹⁸ so that H-abstraction by the above radicals would be



exothermic ($D_{\text{C-H}} = 395^{35}$ and $439^{36} \text{ kJ mol}^{-1}$, respectively, for forming $(\text{CH}_3)_2\text{C}^{\bullet}\text{OH}$ from $(\text{CH}_3)_2\text{C}(\text{OH})\text{-H}$ and CH_3^{\bullet} from $\text{CH}_3\text{-H}$). H-abstraction from the H_2N group of $\text{H}_2\text{NCH}_2\text{CO}_2^-$ is thermodynamically much less favorable ($D_{\text{N-H}} = 406 \text{ kJ mol}^{-1}$).^{18,19} In the case of the zwitterion, where $D_{\text{C-H}}$ is 415 kJ mol^{-1} ,¹⁸ H abstraction from the C-H is also less favorable than from the anion C-H and would be slower.

The yields of CO_2 in these cases are reported relative to the total yields of attacking C-centered radicals. $G_{\text{rel}}(\text{CO}_2)$ for $(\text{CH}_3)_2\text{C}^{\bullet}\text{OH}$ at a dose rate of 54 Gy min^{-1} was found to be 0.31 ± 0.02 over the pH range 7.6–9.5, the independence of pH being similar to that observed for OH^{\bullet} radicals. For CH_3^{\bullet} at the same dose rate, $G_{\text{rel}}(\text{CO}_2)$ was measured only at pH 7.6 and was 0.26. (The individual absolute yields for these systems are available as Supporting Information). Since glycine is the only source of CO_2 in these systems, the observations confirm that those radicals react indeed with this amino acid on the γ -radiolysis time scale. Secondly, since $\text{H}_2\text{N-C}^{\bullet}\text{H-CO}_2^-$ should be the only radical formed, it is evident that it must undergo a reaction (or reactions) which produce CO_2 . In view of the promotion of CO_2 formation by phosphate, observed above, a proton transfer to $\text{H}_2\text{N-C}^{\bullet}\text{H-CO}_2^-$ from a buffer, BH^+ , which

can be either H_2PO_4^- , HPO_4^{2-} , or Gly^{\pm} , is proposed as a straightforward and thus most likely process

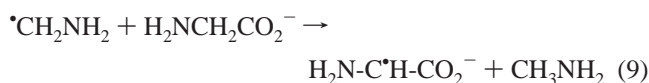


It would immediately be followed by reaction 6 and, accordingly, provide the source of CO_2 . Precedent for protonation of a C-centered radical, that leads to a positive center on a neighboring nitrogen atom, is to be found in the work of Das and von Sonntag.³⁷

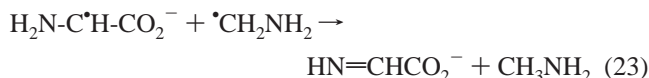
Reaction 22 also has direct relevance to the chain mechanism since it produces a second potential chain carrier, namely, $\text{CH}_2\text{NH}_2^{\bullet}$. The chain then consists of the following components:

Initiation, reactions 1 through 8 and 15; or 1, 2, 19/20, and 21

Propagation, reactions 22, 6, and 9



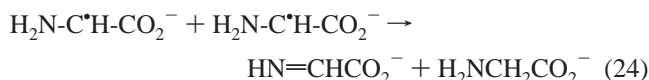
Termination, major reaction only



The nonchain-carrying radicals $\text{HN}^{\bullet}\text{-CH}_2\text{-CO}_2^-$ have been omitted from the termination reactions, and mutual reactions of $\text{CH}_2\text{NH}_2^{\bullet}$ are also not included, since the indications (see below) are that their contributions will be minor. Best fit to the results was in fact obtained with expression VIII

$$G_{\text{rel}}(\text{CO}_2) = 1 + \sqrt{\frac{k_{22}k_9[\text{BH}^+][\text{Gly}^-]}{2k_t}} \frac{1}{\sqrt{\rho}} \quad (\text{VIII})$$

which assumes only the cross termination 23 to be important and where ρ is the rate of radical formation (dose rate $\times 0.1036 \text{ G}$). This reproduces the form of the results for the data of the two upper lines in Figure 6d, with the intercept of unity and slope of $\{k_{22}k_9[\text{BH}^+][\text{Gly}^-]/2k_t\}^{1/2}$. The experimental slopes for the 0.01 and 0.03 M Gly, and the 0.005 M Gly + 0.03 M phosphate yield a mean value of $\{k_{22}k_9/2k_t\}^{1/2} = (1.3 \pm 0.4) \times 10^{-2} \text{ M}^{-0.5} \text{ s}^{-0.5}$. The glycine concentration for the lowest line in Figure 6d is evidently too low for the chain to play a significant role. An analogous expression to VIII, namely $G_{\text{rel}}(\text{CO}_2) = 1 + \{k_{22}[\text{BH}^+]/2k_t\rho\}^{1/2}$, can be developed for reaction 24 as the sole termination process. However, this gave



a factor of two variation in $k_{22}/(2k_t)^{1/2}$, and thus is less satisfactory. One may note here that glyoxylic acid, which is produced in the hydrolysis of the $\text{HN}=\text{CHCO}_2^-$ from reaction 23 (and/or 24), has been observed as a product. A more extensive study of these termination products and other aspects of the chain reaction will be reported elsewhere. While the

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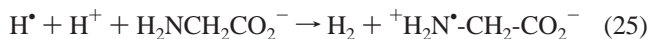
present analysis has made an approximation in considering only the one termination step and in assuming that $^+H_3NCH_2CO_2^-$ and phosphate are equivalent as the proton-transfer agent BH^+ (at pH 10.6), it is evident that the CO_2 -chain yields are consistent with reactions 22 and/or 9 as rate controlling and 6 as a fast step, respectively. Thus, these are the main features of the chain mechanism.

Discussion

Primary Radicals. From the results presented it has become evident that the N-centered $^+H_2N^{\bullet}-CH_2-CO_2^-$ and $HN^{\bullet}-CH_2-CO_2^-$, as well as the C-centered $H_2N-C^{\bullet}H-CO_2^-$ and $^{\bullet}CH_2NH_2$ radicals, are the key players in the decarboxylation and chain-carrying processes, particularly the first three that now will be discussed in length.

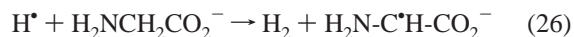
$^+H_2N^{\bullet}-CH_2-CO_2^-$. The most accurate estimate of the yield of $^+H_2N^{\bullet}-CH_2-CO_2^-$ comes from $G_{rel}(CO_2)$ observed in the γ -radiolysis when the chain reaction is suppressed by the presence of scavengers for the chain-carrying radicals. From column two of Table 2 this is seen to be 0.58 for both methyl viologen and $Fe(CN)_6^{3-}$. The co-product of CO_2 , namely $^{\bullet}CH_2NH_2$, will be formed with an identical yield, and it is evident that this must be the major component responsible for the fast reduction of MV^{2+} and $Fe(CN)_6^{3-}$, observed in the pulse-radiolysis experiments. Like all aminium radicals, the $^+H_2N^{\bullet}-CH_2-CO_2^-$ parent will be inherently oxidizing,^{37,38} and it must be converted to $^{\bullet}CH_2NH_2$ before reduction of MV^{2+} or $Fe(CN)_6^{3-}$ can take place. Because of that, the results from the pulse experiments can be used to make an estimate of the rate constant for reaction 6. For the 1 M glycine concentration, that applied to the data for Figure 2, formation of the glycine radicals by $^{\bullet}OH$ would have been completed within the pulse duration (under the described conditions the slowest step was the conversion of e_{aq}^- into $^{\bullet}OH$ through its reaction with N_2O , $t_{1/2}$ ca. 3 ns). As shown in Figure 2, k_{obs} for the formation of $MV^{\bullet+}$ in the fast process was linearly dependent on the MV^{2+} concentration up to the highest measured value of ca. 7×10^7 s $^{-1}$, and there was no curvature to indicate that reaction 6 would become the rate-controlling step at higher $[MV^{2+}]$. Therefore, it can be concluded that the decarboxylation reaction is considerably faster, $k_6 > 10^8$ s $^{-1}$. In support of this, it may be noted that $^+H_2N^{\bullet}-CH_2-CO_2^-$ has never been detected by means of EPR measurements in aqueous solutions,^{16,17,39} and evidence for it was only observed in glycine crystals,⁴⁰ where a $t_{1/2}$ at room temperature of about 1 μ s was reported. From the thermochemical data,¹⁹ the decarboxylation reaction 6 was estimated to be exergonic by 56 kJ mol $^{-1}$.

A point relevant to the consideration of the primary yield of $^+H_2N^{\bullet}-CH_2-CO_2^-$ is that $^{\bullet}OH$ is the only water radical in N_2O -saturated solutions which can produce it. This arises from the fact that reaction 25 is a very unlikely process, especially at



pH 10.6, and H^{\bullet} atoms probably undergo exclusively reaction

26. A second point is that at pH 7, H^{\bullet} reacts very slowly with



glycine, $k_{Gly+H^{\bullet}} = 8 \times 10^4$ M $^{-1}$ s $^{-1}$,²² and even if this were all attributed to Gly^- , $k_{Gly^-+H^{\bullet}}$ would be $\leq 4 \times 10^7$ M $^{-1}$ s $^{-1}$ (about 100 times slower than $k_{Gly^-+^{\bullet}OH}$). Thus, it would appear that H^{\bullet} is unlikely to react quantitatively with Gly^- on the pulse-radiolysis time scale and explains why the values of $G_{rel}(total)$ in column five of Table 2 are less for the pulse- than for the γ -radiolysis experiments (see also below). For both of these reasons it is necessary to know the primary yields of $^+H_2N^{\bullet}-CH_2-CO_2^-$, CO_2 , and $^{\bullet}CH_2NH_2$ relative to $^{\bullet}OH$, as well as those relative to $\{G(^{\bullet}OH) + G(H^{\bullet})\}$. These are referred to as $G_{rel}(OH)(product)$. From the CO_2 yield in the γ -radiolysis experiments with scavengers, the values of $G_{rel}(OH)(CO_2)$, $G_{rel}(OH)(^+H_2N^{\bullet}-CH_2-CO_2^-)$, and $G_{rel}(OH)(^{\bullet}CH_2NH_2)$ are the same and equal to 0.63.

$HN^{\bullet}-CH_2-CO_2^-$. The presence of oxidizing radicals on the pulse-radiolysis time scale was directly demonstrated by their reaction with hydroquinone. Since $^+H_2N^{\bullet}-CH_2-CO_2^-$ is too short-lived, they are identified as $HN^{\bullet}-CH_2-CO_2^-$ radicals. These have to be converted into reductive $H_2N-C^{\bullet}H-CO_2^-$ and $^{\bullet}CH_2NH_2$ forms before being able to react with methyl viologen and $Fe(CN)_6^{3-}$. This conversion, the rate of which is given by the formula for k_{slow} , in expression V, is responsible for the slow formation of reduced products from methyl viologen and $Fe(CN)_6^{3-}$. The yields of $G_{rel}(oxidizing)$ derived from the HQ results and from the "slow yields" with methyl viologen and $Fe(CN)_6^{3-}$, which are listed in column four of Table 2, are in excellent agreement and give an average of 0.34 for $G_{rel}(HN^{\bullet}-CH_2-CO_2^-)$. This corresponds to $G_{rel}(OH)(HN^{\bullet}-CH_2-CO_2^-) = 0.37$.

$H_2N-C^{\bullet}H-CO_2^-$. The values of $G_{rel}(reducing)$ in column three of Table 2, which were derived from the reductions of the two scavengers in the pulse-radiolysis studies, must correspond to the total of $\{G_{rel}(H_2N-C^{\bullet}H-CO_2^-) + G_{rel}(^{\bullet}CH_2NH_2)\}$ formed on the ≤ 100 ns time scale. Since $\{G_{rel}(H_2N-C^{\bullet}H-CO_2^-) + G_{rel}(^{\bullet}CH_2NH_2)\} = 0.59 \pm 0.05$ from the experiments with MV^{2+} is only 0.01 larger than $G_{rel}(^{\bullet}CH_2NH_2) = 0.58 \pm 0.04$ from the CO_2 results and since $\{G_{rel}(H_2N-C^{\bullet}H-CO_2^-) + G_{rel}(^{\bullet}CH_2NH_2)\} = 0.46 \pm 0.05$ for $Fe(CN)_6^{3-}$ is actually smaller, $G_{rel}(H_2N-C^{\bullet}H-CO_2^-)$ in the pulse-radiolysis experiments must in fact be negligible (≤ 0.05). This, in turn, means that reaction 7 is of no importance and that $H_2N-C^{\bullet}H-CO_2^-$ may only be formed via C-centered radicals or H-atoms on a longer time scale. It is also in agreement with the above idea that only few H-atoms react with glycine on that pulse-radiolysis time scale, since a full yield of $H_2N-C^{\bullet}H-CO_2^-$ radicals from reaction 26 would be $G_{rel}(H_2N-C^{\bullet}H-CO_2^-) \approx 0.1$ ($= G(H^{\bullet})/\{G(^{\bullet}OH) + G(H^{\bullet})\}$). For the γ -radiolysis time scale, if one assumes that $G_{rel}(HN^{\bullet}-CH_2-CO_2^-) = 0.34 \pm 0.05$ (from the pulse-radiolysis experiments) and takes $G_{rel}(^+H_2N^{\bullet}-CH_2-CO_2^-) = G_{rel}(^{\bullet}CH_2NH_2) = 0.58 \pm 0.05$ from $G_{rel}(CO_2)$, then there remains a deficit of 0.08. This is within the combined experimental errors of $G_{rel}(HN^{\bullet}-CH_2-CO_2^-)$ and $G_{rel}(CO_2)$, but it does leave room for a $G_{rel}(H_2N-C^{\bullet}H-CO_2^-)$ from reaction 26 of the expected magnitude.

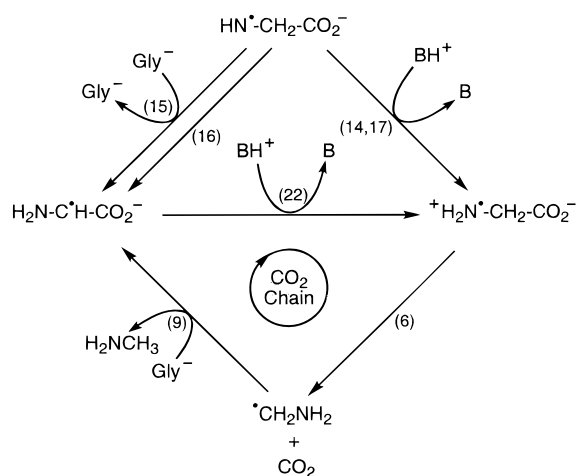
Reactions of $^{\bullet}OH$ with $H_2NCH_2CO_2^-$. The yields for radicals formed from $^{\bullet}OH$ alone are of intrinsic significance and, because of its rapid rate of reaction with glycine anion, would be identical for both γ and pulse-radiolysis time scales. These are $G_{rel}(OH)(^+H_2N^{\bullet}-CH_2-CO_2^-) = G_{rel}(OH)(^{\bullet}CH_2NH_2) = 0.63 \pm 0.05$, $G_{rel}(OH)(HN^{\bullet}-CH_2-CO_2^-) = 0.37 \pm 0.05$, and $G_{rel}(OH)(H_2N-C^{\bullet}H-CO_2^-) \leq 0.05$. Most interesting is the fact

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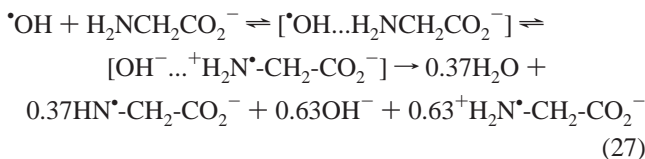
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Scheme 2



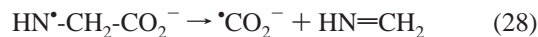
that H-atom abstraction from the α -CH₂ group in H₂NCH₂CO₂⁻, the weakest bond, is entirely dominated by attack at the amino group with formation of ⁺H₂N⁺-CH₂-CO₂⁻ as the major primary process. Whether this occurs by direct electron transfer, reaction 3, or by prior $\sigma\sigma^*$ adduct formation and subsequent OH⁻ elimination, reaction 4 + 5,² is still not clear but, anyway, irrelevant within the context of our present study. Another important process may be H abstraction from the amino group, reaction 8, which is likely to require some activation energy, however. Thus, reaction 3 is possibly the only process, and an associated fast N-H deprotonation occurs in ~37% of the [OH⁻ + ⁺H₂N⁺-CH₂-CO₂⁻] successor pairs to yield HN[•]-CH₂-CO₂⁻ (reaction 27). These points will have to be resolved in future



work.

Secondary Reactions. A major finding of this study was the evidence for relatively facile interconversions of the glycine radicals. The reactions by which these occur have been summarized in the top part of Scheme 2. The deprotonated N-centered HN[•]-CH₂-CO₂⁻ radical anion can be pushed into its ⁺H₂N⁺-CH₂-CO₂⁻ zwitterionic form through the reaction with H⁺/H₂O but also with proton donors like Gly[±] ($k_{14} = 3.9 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$) and phosphate ($k_{17a} = 7.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for H₂PO₄⁻ and $k_{17b} = 2.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for HPO₄²⁻). Thus, the presence of any proton-donating compound would increase the decarboxylation yield by shifting the acid-base equilibrium to the side of the ⁺H₂N⁺-CH₂-CO₂⁻ radicals. While Gly[±] is an effective proton donor, it is unlikely, however, to act as an H-atom donor to HN[•]-CH₂-CO₂⁻ since that reaction would probably be endothermic.^{18,19} For Gly⁻, on the other hand, reaction 15 is estimated to be exothermic by about 43 kJ mol⁻¹, and the formation of the reducing C-centered H₂N-C[•]H-CO₂⁻ radical by that process has, in fact, been demonstrated to occur with $k_{15} = 3.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. Evidence relating to reaction 14a and the intramolecular 1,2-H-atom shift leading to its transformation into the reducing, C-centered H₂N-C[•]H-CO₂⁻ radical (reaction 16) is less certain ($k_{14a}[\text{H}_2\text{O}] + k_{16} = (1.2 \pm 1.0) \times 10^3 \text{ s}^{-1}$). In any case, reaction 16 is also expected to be exothermic by ca. 43 kJ mol⁻¹¹⁹ and therefore feasible. It is noted, though, that a similar 1,2-shift in oxygen-centered alkoxy

radicals occurs faster by about 3 orders of magnitude.⁴¹ Additionally or alternatively, β -fragmentation to yield the CO₂⁻ radical and the HNCH₂ molecule in reaction 28, akin to the



known fragmentation of corresponding alkoxy radicals,^{42,43} might also occur. All aspects concerning the detailed nature of the reactions responsible for the rate constant k_{16} require further work.

The CO₂-Forming Chain Reaction. Certainly the most striking result obtained in the course of this study is the evidence for a chain reaction initiated by C-centered radicals. One possibility could be regeneration of •OH in a reaction of N₂O with strongly reducing radicals (e.g., •CH₂NH₂) as observed in some cases by von Sonntag et al.^{44,45} Thus, we tested systems in which N₂O was absent and replaced by acetone as an electron scavenger, namely, N₂-saturated, 0.03 M glycine, 0.1 M acetone, 1 M 2-propanol, pH 9.0, and N₂-saturated, 0.03 M glycine, 0.01 M acetone, pH 9.5. In the former case, the yield ($G_{\text{rel}}(\text{CO}_2) = 0.34$) is similar to that of 0.31 obtained with 2-propanol and N₂O. In the latter case, the value ($G_{\text{rel}}(\text{CO}_2) = 0.70$) is close to that of 0.76, which is 1/2 of the sum of the yields with N₂O/2-propanol and N₂O alone. These results unambiguously demand the occurrence of a chain process without N₂O involvement and initiated by C-centered radicals. On the other hand, no CO₂ associated with a secondary chain process is observed upon irradiation of N₂O-saturated solutions of α -methylalanine, an amino acid lacking weakly bonded α -amino C-H hydrogens. All of these findings show that any N₂O-mediated chain mechanism cannot be of significance in our systems. Consequently, the major reactions responsible are considered to be those in the bottom part of Scheme 2.

Analysis of the data gave $\{k_{22}k_9/2k_1\}^{1/2} = (1.3 \pm 0.4) \times 10^{-2} \text{ M}^{-0.5} \text{ s}^{-0.5}$, from which $k_{22}k_9/2k_1 = (1.7 \pm 0.8) \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$. Taking a reasonable value of $2k_1 = 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, gives $k_{22}k_9 = (3.4 \pm 0.8) \times 10^5 \text{ M}^{-2} \text{ s}^{-2}$. A rate constant of $120 \text{ M}^{-1} \text{ s}^{-1}$ has been reported for the reaction of •CH₃ with anionic glycine,⁴⁶ and reaction 9 should have a value of about the same magnitude. Thus $k_{22} \approx 3 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$.

Das and von Sonntag³⁷ examined the interconversion of the N- and C-centered radicals of trimethylamine some years ago. That system has no counterpart to the present HN[•]-CH₂-CO₂⁻ radical. However, it is interesting to compare k_{22} with the rate constant for the C-centered protonation of the (CH₃)₂N-C[•]H₂ radical by the (CH₃)₃NH⁺ cation, which has a pK_a (9.76)³⁷ very similar to that of Gly[±]. The rate constant for this process was estimated to be $\sim 3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, which is 2 orders of magnitude larger than k_{22} . There are two probable reasons for that. First the N-centered (CH₃)₃N^{•+} radical has a pK_a of ~ 8 ³⁷ and ΔG for proton addition to (CH₃)₂N-C[•]H₂ under standard conditions is $\Delta G = -55 \text{ kJ/mol}$. The pK_a of the short-lived ⁺H₂N⁺-CH₂-CO₂⁻ is not known experimentally, but a value can be estimated by assuming k_{-22} to be diffusion controlled ($k_{-22} \approx 10^{10} \text{ M}^{-1} \text{ s}^{-1}$). On that basis, and on the basis of the above value of k_{22} and the pK_a of Gly[±], the ⁺H₂N⁺-CH₂-CO₂⁻ pK_a is

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2.9. Thus, ΔG for protonation of $\text{H}_2\text{N}-\text{C}^{\bullet}\text{H}-\text{CO}_2^-$ is +16 kJ/mol. An even more positive value was estimated on theoretical grounds.¹⁹ Thus, reaction 22 is not as favorable energetically as the C-centered protonation of the $(\text{CH}_3)_2\text{N}-\text{C}^{\bullet}\text{H}_2$ species. Second, due to the presence of the carboxylate group, there is more electron delocalization in the $\text{H}_2\text{N}-\text{C}^{\bullet}\text{H}-\text{CO}_2^-$ radical than in $(\text{CH}_3)_2\text{N}-\text{C}^{\bullet}\text{H}_2$, which may also affect the C-protonation process. Electron delocalization has been shown to reduce the rate of carbanion protonation,⁴⁷ and by extrapolation, it is reasonable to assume the same for the protonation of a C-centered radical.

The $^+\text{H}_2\text{N}^{\bullet}-\text{CH}_2-\text{CO}_2^-$ radical that is invoked here as an intermediary in the production of $^{\bullet}\text{CH}_2\text{NH}_2$ and CO_2 is clearly a short-lived unstable species. Thus, one must consider the possibility that reactions 22 and 6 occur as a concerted process and that the $^+\text{H}_2\text{N}^{\bullet}-\text{CH}_2-\text{CO}_2^-$ structure may be only a transition state in the formation of $^{\bullet}\text{CH}_2\text{NH}_2$ and CO_2 via protonation of $\text{H}_2\text{N}-\text{C}^{\bullet}\text{H}-\text{CO}_2^-$. This could also apply for reactions 14 and 6 and 17 and 6. These points and other details of the chain mechanism will have to be resolved by future studies.

Conclusions

The rate of reaction of the $^{\bullet}\text{OH}$ radical with the zwitterion of glycine (Gly^{\pm}) is very slow, and the glycine anion (Gly^-) is the major reactant at pH 7 and above. The primary attack of $^{\bullet}\text{OH}$ radicals on Gly^- seems to occur exclusively at the H_2N group, producing 37% $\text{HN}^{\bullet}-\text{CH}_2-\text{CO}_2^-$ and 63% $^+\text{H}_2\text{N}^{\bullet}-\text{CH}_2-\text{CO}_2^-$ radicals. The latter decompose on a 100-ns or shorter time scale into CO_2 and $^{\bullet}\text{CH}_2\text{NH}_2$. The yields of CO_2 and the reductive $^{\bullet}\text{CH}_2\text{NH}_2$ radicals observed in the earlier work of Mönig *et al.*² in alkaline pH at millimolar glycine concentrations have been confirmed. In addition, it was shown that the N-centered $\text{HN}^{\bullet}-\text{CH}_2-\text{CO}_2^-$ radicals, that are oxidizing in character, can be converted to reducing species. This occurs either by their abstracting hydrogen from the glycine anion to form $\text{H}_2\text{N}-\text{C}^{\bullet}\text{H}-\text{CO}_2^-$ or by their protonation at the nitrogen and subsequent decomposition to CO_2 and $^{\bullet}\text{CH}_2\text{NH}_2$. Thus, in the presence of a sufficiently high Gly^- concentration and/or a proton donor, such as Gly^{\pm} or HPO_4^{2-} , all glycine radicals become reducing on a ms time scale. This was confirmed quantitatively by the bleaching of ferricyanide.

Although there is no evidence for the primary formation of $\text{H}_2\text{N}-\text{C}^{\bullet}\text{H}-\text{CO}_2^-$ by $^{\bullet}\text{OH}$, it was shown that reactions of

$(\text{CH}_3)_2\text{C}^{\bullet}\text{OH}$ and $^{\bullet}\text{CH}_3$ radicals with the glycine anion are a source of CO_2 . That is attributed to H abstraction to form $\text{H}_2\text{N}-\text{C}^{\bullet}\text{H}-\text{CO}_2^-$ and its subsequent protonation at the C-center by the action of buffers, such as Gly^{\pm} or HPO_4^{2-} . This yields CO_2 and $^{\bullet}\text{CH}_2\text{NH}_2$ either via formation of the $^+\text{H}_2\text{N}^{\bullet}-\text{CH}_2-\text{CO}_2^-$ radical, which quickly decomposes, or through a concerted reaction within a transition-state species of similar stoichiometry. In the presence of sufficient buffer and glycine anions, the CO_2 production is a chain reaction that can be suppressed by C-centered radical scavengers and has a yield that depends inversely on the square root of the dose rate. This observation confirms that $^{\bullet}\text{CH}_2\text{NH}_2$ also produces $\text{H}_2\text{N}-\text{C}^{\bullet}\text{H}-\text{CO}_2^-$ by abstracting hydrogen from Gly^- , a reaction previously proposed by Mönig *et al.*² Thus, H abstraction from Gly^- and protonation of the $\text{H}_2\text{N}-\text{C}^{\bullet}\text{H}-\text{CO}_2^-$ C-center are the key chain-carrying reactions, and their rates are sensitive to the Gly^- and proton-donor concentrations, respectively. Gly^{\pm} or HPO_4^{2-} were found to be equally effective in the latter role. In principle, this chain reaction should be initiated by any radical capable of abstracting hydrogen from the Gly^- α -C-atom (center). Also, similar reactions may occur with glycine derivatives having weak α -C-H bonds, and the chain decarboxylation should therefore be of general importance.

Our data and conclusions compare very favorably with a recent publication by Höbel and von Sonntag on the $^{\bullet}\text{OH}$ -induced degradation of EDTA, which appeared while this manuscript was in preparation.⁴⁸

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Supporting Information Available: Tables of experimental data (4 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

JA9815428

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