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## Interaction of Hydrated Electrons with Phenylalanine and Related Compounds

J. P. Mittal and E. Hayon\*<sup>1</sup>

Pioneering Research Laboratory, U. S. Army Natick Laboratories, Natick, Massachusetts 01760 (Received March 27, 1974)

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The reaction rate constants  $k$  of  $e_{aq}^-$  with various phenylalanine peptides and related compounds have been determined by pulse radiolysis at different pH values, taking into consideration the ionization constants of the functional groups present in these molecules. The  $k$  values decrease with deprotonation of the terminal  $-NH_3^+$  groups, and increase with increase in the number of peptide linkages. The interaction of  $e_{aq}^-$  with these peptides is suggested to take place mainly by addition to the carbonyl group of the peptide. Both deamination and addition to the aromatic nucleus has been found to occur. This conclusion was reached based on the observation and identification of the intermediates produced under pulse radiolytic conditions. From the characteristic transient optical absorptions and extinction coefficients of these radicals, it is found that ~40–60% of  $e_{aq}^-$  react with phenylalanine peptides leading to deamination while the remainder add to the aromatic ring. While deamination reactions of aromatic amino acids cannot be readily "repaired," the cyclohexadienyl type of radical produced by  $e_{aq}^-$  addition to the ring followed by protonation could, in principle, be repaired by a one-electron oxidation to an acceptor molecule with a higher (more positive) redox potential than that of the radical.

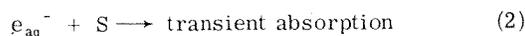
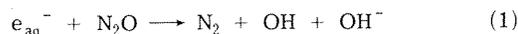
### Introduction

Using the fast-reaction technique of pulse radiolysis and kinetic spectrophotometry, the effects of ionizing radiations on a number of the major constituents of proteins have been studied in this laboratory: amino acids,<sup>2</sup> peptides,<sup>3–6</sup> the peptide linkage,<sup>7</sup> the sulfhydryl group,<sup>8</sup> disulfides,<sup>9</sup> and tyrosine.<sup>10</sup> Reported below are the results obtained from an investigation of the reaction of hydrated electrons with phenylalanine, some phenylalanyl peptides, and related systems in aqueous solution. The extent of reductive deamination *vs.*  $e_{aq}^-$  addition to the aromatic nucleus has been specifically examined. This work was carried out in conjunction with studies on the optical excitation of phenylalanine<sup>11</sup> and phenylglycine<sup>12</sup> in aqueous solutions.

### Experimental Section

The pulse radiolysis set-up used in this work has been described.<sup>13,14</sup> Single pulses of 2.3-MeV electrons and ~30 nsec duration were employed.

The radiation chemistry of water produces  $H_2O \xrightarrow{\gamma} e_{aq}^-$  (2.8), OH(2.8), and H(0.60), where the values in parentheses are  $G$  values (yields of radicals per 100 eV of absorbed energy). The experiments were carried out in argon-saturated aqueous solutions containing *tert*-butyl alcohol to scavenge the OH radicals produced from the radiolysis of water. The  $\beta$  radicals formed from *t*-BuOH absorb<sup>13</sup> below ~280 nm, have a low extinction coefficient, and were found not to interfere with the systems examined here. The concentrations of the substrates used were adjusted such that >90% of the OH radicals react with *t*-BuOH and not with the substrate. The transient optical absorption observed from the reaction of  $e_{aq}^-$  with the substrate disappeared when the solutions were saturated with  $N_2O$  (~2.5  $\times$  10<sup>-2</sup> M), due to competition between reactions 1 and 2



where  $k_1 = 8.7 \times 10^9 M^{-1} \text{sec}^{-1}$  (ref 15).

The chemicals used were the best purity research grade commercially available, and were obtained from Cyclochemicals, Calbiochem, Sigma Chemicals, J. T. Baker, and Mallinckrodt. The solutions were buffered using perchloric acid, potassium hydroxide, and ~1 mM phosphate and tetraborate. The solutions were prepared just prior to irradiation.

Dosimetry was carried out using KCNS as described.<sup>13</sup> Extinction coefficients were derived based on  $G(e_{aq}^-) = G(OH) = 2.8$  and  $G(H) = 0.60$ .

### Results and Discussion

*Reactivity toward  $e_{aq}^-$ .* The reaction rate constants of  $e_{aq}^-$  with phenylalanine and related compounds were determined in solutions containing 0.1–1.0 M *t*-BuOH by following the decay kinetics of  $e_{aq}^-$  at 700 nm. From the pseudo-first-order rates, the second-order rates were determined. These are given in Table I and ref 15 and 16. These rates were determined at the appropriate pH values taking into account the ionization constants ( $pK_a$ ) of the substrates.

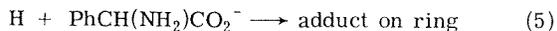
The presence of a protonated amino group,  $-NH_3^+$ , as in benzylamine, phenylalanine (Phe), phenylalaninamide (Phe-NH<sub>2</sub>), and the glycine peptides of phenylalanine increases the reactivity toward  $e_{aq}^-$  as compared to the ionized  $-NH_2$  group. This effect has also been observed<sup>3,4,7,17</sup> for simple amino acids and peptides. It is interesting to note that the presence of a  $-CO_2^-$  group increases the rate:  $k = 1.6 \times 10^8 M^{-1} \text{sec}^{-1}$  for PhCH<sub>2</sub>NH<sub>2</sub> compared to  $3.0 \times 10^8 M^{-1} \text{sec}^{-1}$  for PhCH(NH<sub>2</sub>)CO<sub>2</sub><sup>-</sup>. In the absence of an amino group,  $k = 2.0 \times 10^7 M^{-1} \text{sec}^{-1}$  for PhCH<sub>2</sub>CO<sub>2</sub><sup>-</sup> and  $k = 1.2 \times 10^7 M^{-1} \text{sec}^{-1}$  for toluene.<sup>15</sup> When the amino group is on the  $\beta$  carbon (with respect to the benzene ring), as in phenylalanine, the reactivity toward  $e_{aq}^-$  decreases further. It is clear that benzyl derivatives interact more strongly with the benzene ring. This is based on both their reaction with  $e_{aq}^-$  and their spectroscopic properties. Glycine, alanine, and benzene react relatively slowly<sup>15</sup> with

$e_{aq}^-$ , while the rate is considerably higher with phenylglycine and phenylalanine.

The formation of peptide groups as in Phe-NH<sub>2</sub>, Gly-Phe, Gly-Phe-Gly, Phe-Gly-Gly, and Gly-Gly-Phe increases the reactivity of these molecules, as observed earlier<sup>4,7</sup> for aliphatic peptides. Ionization (loss of proton) of the -NH<sub>3</sub><sup>+</sup> group has a relatively smaller effect (Table I) with aromatic peptides compared to aliphatic peptides, since the peptide linkages and the aromatic ring interact strongly with  $e_{aq}^-$ . The highest rate observed,  $\sim 2 \times 10^9 M^{-1} \text{ sec}^{-1}$ , is still appreciably lower than diffusion-controlled limits.

### Phenylglycine and Derivatives

The pulse radiolysis of  $10^{-2} M$  phenylglycine (in presence of  $1.5 M$  *t*-BuOH) at pH 9.0 in the presence of argon (1 atm) produces a transient absorption with a  $\lambda_{\text{max}}$  282 nm, see Figure 1. On saturation of the aqueous solution with N<sub>2</sub>O, all the  $e_{aq}^-$  react *via* reaction 1 and a relatively weak absorption is obtained with  $\lambda_{\text{max}} \sim 322$  nm. The following reactions are suggested



Support for the deamination reaction (3) was obtained by producing the Ph $\dot{\text{C}}\text{HCO}_2^-$  radical by an independent reaction. Figure 2 shows the transient spectra obtained from the reaction of  $e_{aq}^-$  with  $\alpha$ -chlorophenylacetic acid



Dechlorination of compounds by  $e_{aq}^-$  is well known<sup>18</sup> and produces specific radicals. Based on  $\epsilon_{282} 3.3 \times 10^4 M^{-1} \text{ cm}^{-1}$  for the Ph $\dot{\text{C}}\text{HCO}_2^-$  radical, derived *via* reaction 6, it is found that  $90 \pm 5\%$  of  $e_{aq}^-$  deaminate phenylglycine *via* reaction 3. The remaining  $e_{aq}^-$  presumably add to the benzene ring. The weak spectrum observed in N<sub>2</sub>O solutions (Figure 1) is the H-atom adduct to phenylglycine. An identical spectrum was observed on pulse radiolysis of phenylglycine at pH 0.4, when all the  $e_{aq}^-$  were converted to H atoms



and these atoms predominantly add to phenylglycine. An  $\epsilon_{322} \sim 8 \times 10^3 M^{-1} \text{ cm}^{-1}$  was obtained. At this pH both the amino and carboxyl groups are protonated.

The Ph $\dot{\text{C}}\text{HCO}_2^-$  radical can be protonated and a  $pK_a$  of  $5.5 \pm 0.1$  was observed (see Figure 2) for its acid-base equilibrium.



This value is to be compared to  $pK_a = 4.3$  for phenylacetic acid. This difference is consistent with that observed for other carboxylic acid radicals (see ref 19). Based on  $\epsilon_{262} 3.3 \times 10^4 M^{-1} \text{ cm}^{-1}$  for the Ph $\dot{\text{C}}\text{HCO}_2^-$  radical, excellent agreement was obtained for the second-order decay of this radical produced *via* reactions 3 and 6,  $2k = 1.3 \times 10^9 M^{-1} \text{ sec}^{-1}$  (see Table II).

On reaction of  $e_{aq}^-$  with *N*-acetylphenylglycine, no deamination can occur and essentially all the  $e_{aq}^-$  add to the benzene ring (see Table III).

The reaction of benzylamine ( $pK_a = 9.3$ ) with  $e_{aq}^-$  at pH 7.5 gives rise to a transient spectrum with maxima at 318

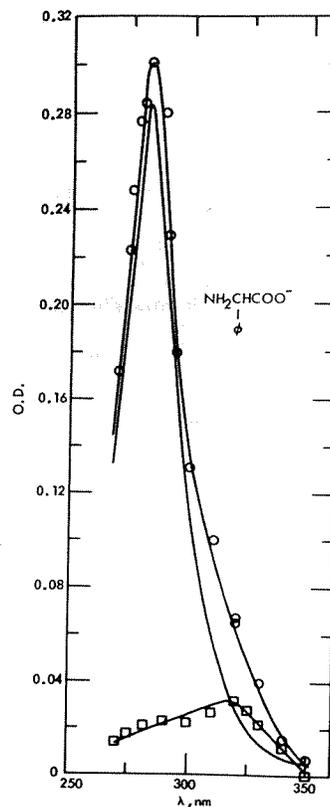


Figure 1. Absorption spectrum of the Ph $\dot{\text{C}}\text{HCO}_2^-$  radical produced from the reductive deamination by  $e_{aq}^-$  of phenylglycine ( $1 \times 10^{-2} M$ , pH 9.0, in presence of  $1.5 M$  *t*-BuOH, Ar (O), and N<sub>2</sub>O (□)). Full line is difference spectrum. Total dose  $\sim 1.2$  krad/pulse.

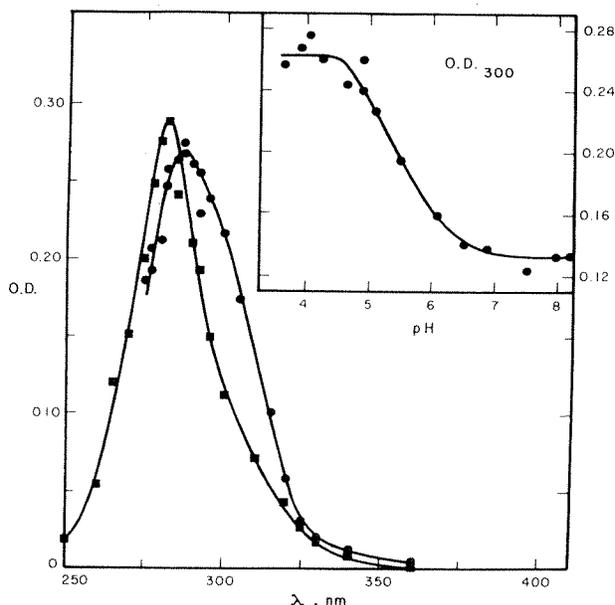


Figure 2. Absorption spectra of the Ph $\dot{\text{C}}\text{HCOOH}$  (●) and Ph $\dot{\text{C}}\text{HCO}_2^-$  (■) radicals produced from the reaction of  $e_{aq}^-$  with  $\alpha$ -chlorophenylacetic acid ( $1.2 \times 10^{-2} M$ , in presence of  $2.0 M$  *t*-BuOH). The insert shows the change in absorbance at 300 nm with pH. Total dose  $\sim 1.3$  krad/pulse.

and 307 nm, qualitatively similar to the spectrum for the benzyl radical reported<sup>20</sup> recently. Based on the  $\epsilon_{318} 9.0 \times 10^3 M^{-1} \text{ cm}^{-1}$  for the Ph $\dot{\text{C}}\text{H}_2$  radical, it was found that  $\sim 60\%$  of the  $e_{aq}^-$  lead to deamination

**TABLE I: Reaction Rate Constants of  $e_{aq}^-$  with Phenylalanine Peptides and Related Compounds in Aqueous Solution**

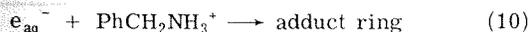
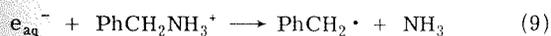
Compound	$pK_a$	pH	Ionic form	$k(e_{aq}^- + S), M^{-1} sec^{-1}^a$
Phenylacetic acid	4.3	9.0	$PhCH_2CO_2^-$	$2.0 \times 10^7 (4.1 \times 10^7)$
$\alpha$ -Chlorophenylacetic acid		9.2	$PhCH(Cl)CO_2^-$	$2.7 \times 10^9$
Benzylamine	9.3	6.9	$PhCH_2NH_3^+$	$8.0 \times 10^8 (1.5 \times 10^9)^b$
		10.9	$PhCH_2NH_2$	$1.6 \times 10^8 (3.4 \times 10^7)^b$
$\beta$ -Chlorophenylethane		9.2	$PhCH_2CH_2Cl$	$6.0 \times 10^8$
Phenylglycine	1.8, 4.9	9.2	$PhCH(NH_2)CO_2^-$	$3.0 \times 10^8$
<i>N</i> -Acetylphenylglycine		9.2	$PhCH(NHCOCH_3)-CO_2^-$	$1.7 \times 10^8$
Phenylalanine	1.8, 9.1	6.9	$+H-Phe-O^-$	$1.6 \times 10^8 (1.5 \times 10^8)$
		11.2	$Phe-O^-$	$(1.4 \times 10^7)$
<i>N</i> -Acetylphenylalanine		9.2	$Ac-Phe-O^-$	$5.3 \times 10^7$
Phenylalaninamide	7.2	5.4	$+H-Phe-NH_2$	$1.4 \times 10^9$
		9.2	$Phe-NH_2$	$1.4 \times 10^8$
<i>N</i> -Acetylphenylalaninamide		9.3	$Ac-Phe-NH_2$	$2.5 \times 10^8$
Glycylphenylalanine	3.1, 8.2	5.9	$+H-Gly-Phe-O^-$	$6.1 \times 10^8 (1.6 \times 10^8)$
		9.4	$Gly-Phe-O^-$	$1.3 \times 10^8$
<i>N</i> -Chloroacetylphenylalanine		9.2	$ClCH_2CO-Phe-O^-$	$2.3 \times 10^9$
Glycylphenylalanyl-glycine		5.5	$+H-Gly-Phe-Gly-O^-$	$1.6 \times 10^9$
		11.6	$Gly-Phe-Gly-O^-$	$5.4 \times 10^8$
Phenylalanyl-glycyl-glycine		6.6	$+H-Phe-Gly-Gly-O^-$	$1.1 \times 10^9$
		11.3	$Phe-Gly-Gly-O^-$	$3.7 \times 10^8$
Glycylglycylphenylalanine		6.1	$+H-Gly-Gly-Phe-O^-$	$1.2 \times 10^9$
		9.1	$Gly-Gly-Phe-O^-$	$3.8 \times 10^8$

<sup>a</sup> Values to  $\pm 10\%$ ; rates obtained from two to three concentrations of the substrates; values in parentheses from ref 15. <sup>b</sup> From ref 16.

**TABLE II: Absorption Maxima, Extinction Coefficients, and Decay Kinetics of Radicals Produced from the Reaction of  $e_{aq}^-$  with Phenylalanine and Related Compounds**

Compound	pH	Radical	$\lambda_{max}, nm$	$\epsilon_{max}, M^{-1} cm^{-1}$	$2k, M^{-1} sec^{-1}$
Phenylglycine	9.0	$Ph\dot{C}HCO_2^-$	282		$1.3 \times 10^9$
$\alpha$ -Chlorophenylacetic acid	9.2	$Ph\dot{C}HCO_2^-$	282	$3.3 \times 10^4$	$1.3 \times 10^9$
	3.8	$Ph\dot{C}HCO_2H$	287	$3.7 \times 10^4$	
Benzylamine	7.5	$Ph\dot{C}H_2$	318	$9.0 \times 10^{3a}$	$5.1 \times 10^9$
Phenylalanine	5.3	$e_{aq}^-$ adduct	325 <sup>b</sup>		
Glycylphenylalanine	5.9	$\dot{C}H_2CONH-Phe-O^-$	435		$1.1 \times 10^{9c}$
<i>N</i> -Chloroacetylphenylalanine	9.2	$\dot{C}H_2CONH-Phe-O^-$	435	$1.3 \times 10^3$	$4.2 \times 10^8$
Glycylphenylalanyl-glycine	5.5	$\dot{C}H_2CONH-Phe-Gly-O^-$	435		$9.0 \times 10^{8c}$

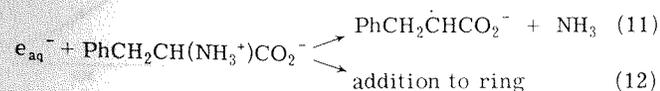
<sup>a</sup> From ref 20. <sup>b</sup> Absorption band contains contribution from the H atom adduct. <sup>c</sup> Based on  $\epsilon_{435} 1.5 \times 10^3 M^{-1} cm^{-1}$ .



On pulse radiolysis of benzylamine solutions at pH 11.5, only a very small fraction (<10%) of  $e_{aq}^-$  appear to deaminate, i.e., most of the electrons add to the benzene ring to form substituted cyclohexadienyl radicals.

### Phenylalanine and Derivatives

The interaction of  $e_{aq}^-$  with phenylalanine may result in both deamination and addition to the aromatic nucleus



The  $PhCH_2\dot{C}HCO_2^-$  radical is expected<sup>21</sup> to have a low extinction coefficient and to start absorbing below  $\sim 350$  nm. The transient optical absorption spectrum observed is shown in Figure 3a. In the presence of  $N_2O$ , a similar spectrum is observed due to the H-atom adduct, for which  $\epsilon_{325} \sim 1 \times 10^4 M^{-1} cm^{-1}$  can be estimated.

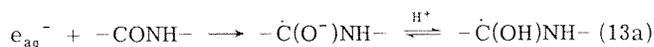
The reaction of  $e_{aq}^-$  with *N*-acetylphenylalanine gives mainly an  $e_{aq}^-$  adduct (Figure 3b), with an  $\epsilon_{325} \sim 1.2 \times 10^4 M^{-1} cm^{-1}$ . Based on this extinction coefficient, and assum-

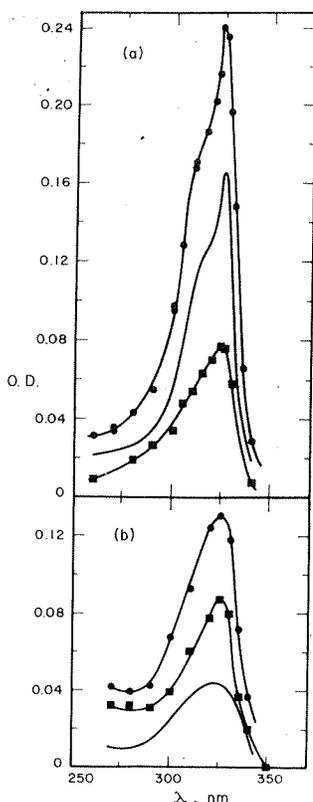
**TABLE III: Interaction of  $e_{aq}^-$  with Phenylalanine Peptides and Related Compounds. Deamination vs. Addition Reactions**

Compound	pH	% deamination	% addition
Phenylglycine	9.0	$90 \pm 5$	$10 \pm 5$
<i>N</i> -Acetylphenylglycine	9.2	0	$\sim 100$
Benzylamine	7.5	$\sim 60 \pm 10$	$\sim 40 \pm 10$
	11.5	$\sim 10 \pm 10$	$\sim 90 \pm 10$
Phenylalanine	6.9	$\sim 50 \pm 10$	$\sim 50 \pm 10$
<i>N</i> -Acetylphenylalanine	9.2	0	$\sim 100$
Phenylalaninamide	6.2	$\sim 60 \pm 10$	$\sim 40 \pm 10$
Glycylphenylalanine	5.9	$50 \pm 5$	$50 \pm 5$
Glycylphenylalanyl-glycine	5.5	$40 \pm 5$	$50 \pm 5$
Phenylalanyl-glycyl-glycine	6.1	$55 \pm 10$	$45 \pm 10$
Glycylglycylphenylalanine	5.7	$45 \pm 10$	$55 \pm 10$

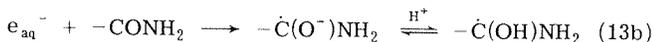
ing that the  $\epsilon$  for the  $e_{aq}^-$  adduct to Phe to be the same as that of *N*-acetylphenylalanine (with no contribution from the  $PhCH_2\dot{C}HCO_2^-$  radical at 325 nm), one concludes that  $\sim 50 \pm 10\%$  of  $e_{aq}^-$  react *via* reaction 11, the remainder presumably add to the benzene ring.

Hydrated electrons have been shown to add to peptide linkages<sup>4,5,7</sup> and to amide groups<sup>22</sup> to produce ketyl-type radicals





**Figure 3.** Transient spectra produced from the reaction of  $e_{aq}^-$  with (a) phenylalanine (5 mM, 1.5 M *t*-BuOH) at pH 6.9 in presence of Ar (●) and  $N_2O$  (■) (Difference spectrum is shown as a full line. Total dose  $\sim 6.5$  krads/pulse.) (b) *N*-acetylphenylalanine (10 mM, 1.5 M *t*-BuOH) at pH 9.2 in presence of Ar (●) and  $N_2O$  (■) (Difference spectrum is shown as full line. Total dose  $\sim 8.0$  krads/pulse.).

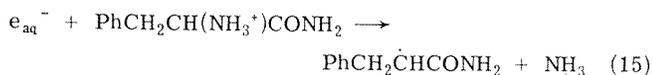


and also to lead to deamination



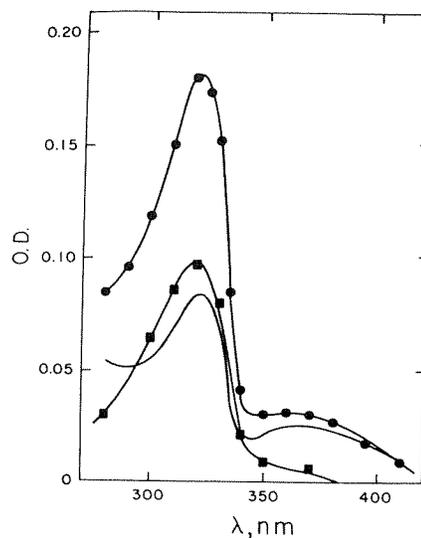
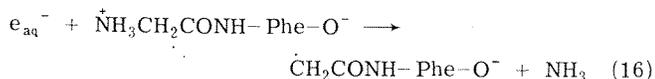
The  $-\dot{C}(OH)NR_2$  radicals<sup>22</sup> and the  $-\dot{C}(OH)NH-$  radicals<sup>7</sup> have relatively low extinction coefficients, absorb in the far-uv region, and have high  $pK_a$  values. The  $\dot{C}H_2CONH_2$  radicals<sup>4</sup> have  $\epsilon \sim 1100 M^{-1} cm^{-1}$  and absorption maxima in the range 350–450 nm, depending on the nature of the substituents on the C- and N- atoms.

The transient spectrum observed on reaction of  $e_{aq}^-$  with phenylalaninamide is shown in Figure 4. The absorption at  $\sim 320$  nm is clearly due to the  $e_{aq}^-$  adduct with a relatively low apparent  $\epsilon$ . In addition, the species with  $\lambda_{max} \sim 370$  nm is presumably the radical  $PhCH_2\dot{C}HCONH_2$  formed by deamination

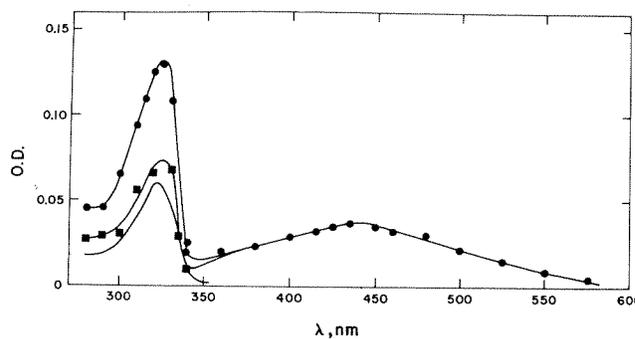


Taking  $\epsilon 1100 M^{-1} cm^{-1}$  for this radical, one can calculate that  $\sim 60 \pm 10\%$  of the  $e_{aq}^-$  lead to deamination of phenylalaninamide.

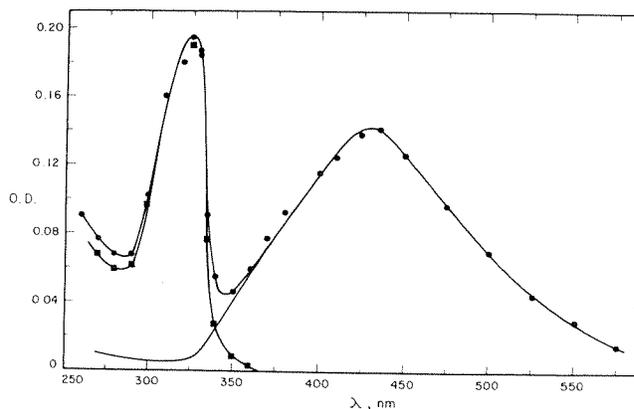
**Glycylphenylalanine.** The interaction of  $e_{aq}^-$  with this peptide leads to deamination and addition reactions. Figure 5 shows the transient spectra obtained.



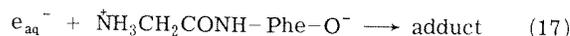
**Figure 4.** Transient spectra produced from the reaction of  $e_{aq}^-$  with phenylalaninamide ( $10^{-2}$  M, 1.5 M *t*-BuOH) at pH 6.2 in presence of Ar (●) and  $N_2O$  (■). Full line is the difference spectrum. Total dose  $\sim 8.5$  krads/pulse.



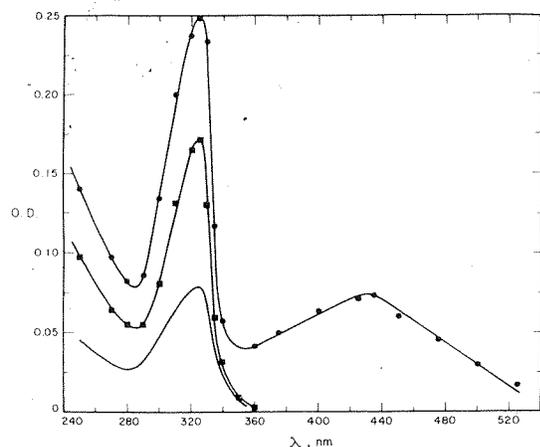
**Figure 5.** Transient spectra produced from the reaction of  $e_{aq}^-$  with glycylphenylalanine (3 mM, 1.5 M *t*-BuOH) at pH 5.9 in presence of Ar (●) and  $N_2O$  (■). Full line is the difference spectrum. Total dose  $\sim 9.5$  krads/pulse.



**Figure 6.** Transient spectra produced from the reaction of  $e_{aq}^-$  with *N*-chloroacetylphenylalanine (4 mM, 1.5 M *t*-BuOH) at pH 9.2 in presence of Ar (●) and  $N_2O$  (■). Total dose  $\sim 19$  krads/pulse.



The  $\dot{C}H_2CONH-Phe-O^-$  radical was produced from the reaction of  $e_{aq}^-$  with *N*-chloroacetylphenylalanine, Figure 6. A maximum at  $\lambda 435$  nm was found and an  $\epsilon_{435} 1.3 \times 10^3$



**Figure 7.** Transient spectra produced from the reaction of  $e_{aq}^-$  with glycyphenylalanylglycine (2.4 mM, 1.5 M *t*-BuOH) at pH 5.5 in presence of Ar (●) and  $N_2O$  (■). Difference spectrum is shown as full line. Total dose  $\sim 19$  krad/pulse.

$M^{-1} \text{ cm}^{-1}$ . Based on this  $\epsilon$ ,  $\sim 50\%$  of the electrons are found to react *via* reaction 16. The transient with  $\lambda_{\text{max}}$  325 nm in Figure 6 is mainly the H atom adduct to *N*-chloroacetyl-phenylalanine.

*Glycyphenylalanylglycine.* Similar results are obtained for this peptide, see Figure 7 and Table III. The reaction of  $e_{aq}^-$  with phenylalanylglycylglycine and with glycyglycyl-phenylalanine result in both deamination and addition to the aromatic nucleus (Table III, transient spectra not shown).

### Conclusion

The results presented above conclusively show that reductive deamination of phenylalanine and its peptides by  $e_{aq}^-$  is an important process. The data indicate that  $\sim 40\text{--}60\%$  of the hydrated electrons lead to the deamination of

simple oligopeptides of phenylalanine. The remaining  $e_{aq}^-$  apparently all add to the aromatic ring. Similar  $e_{aq}^-$  addition to the aromatic nucleus of phenolic compounds and tyrosine has been found.<sup>10</sup> While deamination reactions of aromatic amino acids are damaging (*i.e.*, no "repair" of the molecule can be brought about), addition reactions to the aromatic nucleus could, under certain conditions, be "repaired." Such a restoration of the original molecule can occur by one-electron oxidation of the substituted cyclohexadienyl type of radical in the presence of electron acceptors having a higher (more positive) redox potential. The kinetic redox potential of the electron adduct to phenylalanine has been determined and is relatively high (positive).<sup>23</sup>

### References and Notes

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