UCRL-17285

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CHEMISTRY OF THE HYDRATED ELECTRON IN OXYGEN-FREE SOLUTIONS OF AMINO ACIDS, PEPTIDES, AND RELATED COMPOUNDS

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Submitted to:
Radiation Research

UCRL-17285
Preprint

UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

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Rodney L. S. Willix and Warren M. Garrison

November 1966

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Rodney L. S. Willix and Warren M. Garrison, Chemistry of the Hydrated Electron in Oxygen-Free Solutions of Amino Acids, Peptides, and Related Compounds Radiation Res. ___ pp. __ __, ___.

ABSTRACT

In extending previous studies on the radiation-induced deamination of the simpler α-amino acids in oxygen-free solution it has been found that reductive deamination by the hydrated electron, e^-_{aq}, is not confined to the free amino-acid configuration. The dipeptides, tripeptides, and other derivatives of glycine for example are found to react with e^-_{aq} (essentially quantitatively) to cleave the N-C bond of the primary amino group. Radiolysis studies of variously substituted amino compounds in solutions containing second solutes which are specific scavengers of H,OH in the one case and of e^-_{aq} in the other indicates that reductive deamination by e^-_{aq} requires an unsaturated function at the carbon position α to the amino group. It is suggested that e^-_{aq} adds to this function and that N-C cleavage then ensues. Observed correlations between rates of reaction of e^-_{aq} and pK of the amino group are in accord with this formulation. Velocity constants for reaction of e^-_{aq} with amino acids and derivatives in both acidic and neutral solution were obtained by the method of competition kinetics.

Hydrated electron, amino acids, reductive deamination, reaction rates

INTRODUCTION

Recent work (1,2) has shown that the hydrated electron, e^-_{aq}, which is formed in the radiation-induced decomposition of water (3-5)

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

reacts with both the zwitterion and cation forms of the simplest α-amino acids, glycine and alanine, via the reductive deamination reaction

$$e^-_{aq} + NH_3^+CHR_2 \longrightarrow NH_3 + \dot{C}HR_2 \qquad (2a)$$

and to a lesser extent through the conversion reaction

$$e^-_{aq} + NH_3^+CHR_2 \longrightarrow H + NH_2CHR_2 \qquad (2b)$$

In acidic solution, reactions 2a, 2b occur in competition with

$$e^-_{aq} + H_3O^+ \longrightarrow H + H_2O \qquad (3)$$

The radicals OH and H react with both glycine and alanine through hydrogen abstraction at the α-carbon position

$$OH + NH_3^+CHR_2 \longrightarrow H_2O + NH_3^{+\cdot}CR_2 \qquad (4)$$

$$H + NH_3^+CHR_2 \longrightarrow H_2 + NH_3^{+\cdot}CR_2 \qquad (5)$$

which reactions are followed by the oxidative deamination steps[3] (1,2,6)

$$NH_3^+CR_2 + \dot{C}HR_2 \longrightarrow NH_2^+{=}CR_2 + CH_2R_2 \qquad (6)$$

$$2\ NH_3^+\dot{C}R_2 \longrightarrow NH_2^+{=}CR_2 + NH_3^+CHR_2 \qquad (7)$$

$$H_2O + NH_2^+{=}CR_2 \longrightarrow NH_4^+ + R_2CO \qquad (8)$$

By introducing second solutes which are specific scavengers for OH and H in the one case and for e^-_{aq} in the other, it has been possible to separately evaluate the oxidative and reductive modes of deamination of the simpler α-amino acids (2).

We report here an extension of this earlier work to include other more complex biochemical substances containing primary and secondary amino functions. Effects of pH and of chemical composition on the various modes of reaction of e^-_{aq} are described. Velocity constants for reaction of e^-_{aq} with these organo-nitrogen compounds are derived from measurements of competition kinetics in two-solute systems.

EXPERIMENTAL

The organo-nitrogen compounds (Nutritional Biochemicals) with the exception of N-ethylacetamide (Eastman) were recrystallized from distilled water a minimum of two times. The N-ethyl acetamide was redistilled in vacuo as was the chloracetic acid (Eastman). Water from a Barnstead still,

redistilled first from alkaline permanganate and then from sulfuric acid was used in the preparation of the solutions. All other chemicals were of reagent grade. The pH adjustments were made with sulfuric acid or sodium hydroxide.

The pyrex irradiation cells containing 10 ml of solution were degassed on the vacuum line, sealed-off, and irradiated with Co^{60} γ rays at a dose rate of 1.6×10^{18} eV/gm/min as determined with the Fricke dosimeter [$G(Fe^{+++}) = 15.5$, $\epsilon_{305} = 2180$ at 24°C]. Dosage did not exceed 1.5×10^{19} eV/gm; dose-yield relationships were linear over this range.

The Conway diffusion method[7] was used to separate ammonia from the irradiated solutions. Diffusates were assayed by means of Nessler reagent. Chloride ion was determined by the method of Luce et al. (8) after Hayon and Allen (9). The appropriate blank and control runs were made. Ammonia and chloride measurements were reproducible to within ~5%.

RESULTS AND DISCUSSION

Reaction Rates

Rate constants for reaction of e^-_{aq} with the substances listed in Table I were derived from an analysis of competitive kinetics involving the organo-nitrogen compound at a fixed concentration, 0.05 M,

$$e^-_{aq} + R_3N \longrightarrow \text{product} \qquad (9)$$

and a second solute, chloracetic acid, in increasing concentration over the range $\sim 5 \times 10^{-4}$ M to $\sim 5 \times 10^{-2}$ M. The latter reacts with e^-_{aq} according to the stoichiometry (9,12)

$$e^-_{aq} + RCl \longrightarrow R + Cl^- \qquad (10)$$

to give chloride ion which product is followed analytically. No assumptions regarding the nature of reaction 9 are involved in the rate studies.

All the compounds studied have pK values such that at pH 7 each solute exists almost exclusively as a single species, i.e., the zwitterion form of the α-amino acids, β-amino acids, and dipeptides, the cation form of the simple amines, and the anion forms of the acetylamino acids and the chloroacetic acid. For simplicity we distinguish these proton-deficient species in terms of $\overline{R_3N}$ and $\overline{RCl}$ as defined by the equilibria

$$(\overline{R_3N})(H^+)/(R_3N) = K_{R_3N}$$

$$(\overline{RCl})(H^+)/(RCl) = K_{RCl}$$

The reactions in neutral solution then are written

$$\overline{R_3N} + e^-_{aq} \longrightarrow \text{products} \qquad (\overline{9})$$

$$\overline{RCl} + e^-_{aq} \longrightarrow \overline{R} + Cl^- \quad , \qquad (\overline{10})$$

to distinguish from the corresponding reaction of the acid forms given by Eqs. 9 and 10 For simple competition in these two solute systems at pH 7 we may derive the expression

$$\frac{1}{G(Cl^-)} = \frac{1}{G_{e^-_{aq}}} + \frac{1}{G_{e^-_{aq}}}\left(\frac{\overline{k}_9}{\overline{k}_{10}}\right)\left(\frac{\overline{R_3N}}{\overline{RCl}}\right) , \qquad (11)$$

where $G(Cl^-)$ represents the experimentally observed chloride yield, $(\overline{R_3N})$ and $(\overline{RCl})$ the concentrations of the two solute-species in neutral solution, and $\bar{k}_9$ and $\bar{k}_{10}$ the respective velocity constants for their reaction with e^-_{aq}. A plot of the reciprocal of the chloride yield as a function of $(\overline{R_3N})/(\overline{RCl})$ gives a straight line with slope $(1/G_{e^-_{aq}})(\bar{k}_9/\bar{k}_{10})$, as shown by the typical data of Fig. 1.

The intercept value $1/G(Cl^-) = 0.36$ gives $G_{e^-_{aq}} \approx 2.8$, in good agreement with published values (5,10). Taking $\bar{k}_{10} = 1.2 \times 10^9\ M^{-1}\ sec^{-1}$ as determined by Anbar and Hart (11) in pulse radiolysis studies, we obtain the values of $\bar{k}_9$ given in Table I.

A parallel series of experiments was run at pH 3 to obtain rate constants for reactions of e^-_{aq} with these organo-nitrogen compounds in the protonated form. Results are obtained in terms of the rate constant for reaction of e^-_{aq} with the undissociated chloracetic acid molecule. Corrections must be included for removal of e^-_{aq} by the proton reaction 3 , $k_3 = 2.2 \times 10^{10}\ M^{-1}\ sec^{-1}$, and for the competition by $\overline{R_3N}$ and $\overline{RCl}$ at the concentrations determined by the equilibrium constants K_{R_3N}, K_{RCl}. It can be shown that Eq. 11 then takes the more complicated form

$$\frac{1}{G(Cl^-)} = \frac{1}{G_{e^-_{aq}}} + \frac{1}{G_{e^-_{aq}}} \left\{ \frac{k_9(H^+) + \bar{k}_9 K_{R_3N} + k_3(H^+)^2/(R_3N)}{k_{10}(H^+) + \bar{k}_{10} K_{RCl}} \right\} \left(\frac{R_3N}{RCl} \right) . \quad (13)$$

Here again a plot of the reciprocal chloride ion yield versus $(R_3N)/(RCl)$ should give a straight line with intercept equal to $1/G_{e^-_{aq}}$. From the slopes given by

$$\frac{1}{G_{e^-_{aq}}} \left\{ \frac{k_9(H^+) + \bar{k}_9 K_{R_3N} + k_3(H^+)^2/(R_3N)}{k_{10}(H^+) + \bar{k}_{10} K_{RCl}} \right\}$$

We may calculate the respective values of k_9, assuming $k_{10} = 6.6 \times 10^9\ M^{-1}\ sec^{-1}$ as derived from the work of Hayon and Allen (9). Values of k_9 so obtained are listed in Table I.

Some of the rate constants reported in Table I have also been measured by pulse-radiolysis methods in which e^-_{aq} is followed spectrophotometrically (13,14). The latter values are included in parentheses under $\bar{k}_9$ in Table I, and as can be seen the agreement between the two methods is reasonably good. Rate constants for reaction of e^-_{aq} with the cation forms of the amino acids and simple peptides (k_9) are not available as yet from pulse-radiolysis work. Presumably this is because of the very short life-time of e^-_{aq} in aqueous solution at the low pH values needed to retain an appreciable fraction of these solutes in the cation form. At pH 3, for example, assuming $k_3 = 2 \times 10^{10}\ M^{-1}\ sec^{-1}$ the life-time of e^-_{aq} corresponds to $1/(10^{-3})(2 \times 10^{10}) = 0.5 \times 10^{-7}$ sec.

Chemical Criteria for Reductive Deamination by e^-_{aq}.

We found in the earlier work (1,2) that the yield for reductive deamination of glycine and alanine via reaction 2a could be separately measured through use of a second solute such as formate ion which reacts rapidly with OH and H

$$OH + HCOO^- \longrightarrow H_2O + COO^- \qquad (14)$$

$$H + HCOO^- \longrightarrow H_2 + \cdot COO^- \qquad (15)$$

$k_{14} = 10^9\ M^{-1}\ sec^{-1}$, $k_{15} = 2 \times 10^8\ M^{-1}\ sec^{-1}$ but is relatively unreactive towards e^-_{aq}

$$e^-_{aq} + HCOO^- \longrightarrow HCOO^{2-} \qquad (16)$$

$k_{16} = < 10^5\ M^{-1}\ sec^{-1}$ (15). The preferential scavenging of OH and H via reactions 14 and 15 blocks the formation of the α-carbon radicals $NH_3^{+\cdot}CR_2'$ which in the absence of formate yield ammonia and carbonyl via steps 6-8 . Hence at sufficiently high formate concentrations the observed $G(NH_3)$ value provides a direct measure of reaction 2a.

We have found, in applying this technique to other systems, that reductive deamination via reaction 2a is not unique to the free α-amino acid configuration. In evaluating the experimental evidence it is convenient here first to compare the ammonia yields from glycine and from the dipeptide glycylglycine at pH 7 in oxygen-free solution under γ rays. We observe, Fig. 2, that $G(NH_3)$ from both compounds increase abruptly with solute concentration and approach limiting yields under which conditions we may assume that all of the OH, H, e^-_{aq} formed in the radiation-induced reaction are quantitatively scavenged by the solute. The effects of added formate ion on these maximal ammonia yields from glycine and glycylglycine are shown in Fig. 3. In both cases $G(NH_3)$ decreases with increasing formate concentrations and then levels off to a limiting value which remains essentially constant at the higher formate concentrations. With glycine, the ammonia yield levels off to give $G(NH_3) = 1.8$ as a measure of the reductive deamination reaction 2a in this system; the yield for conversion of e^-_{aq} to H through reaction 2b corresponds

to $G_{e^-_{aq}} - 1.8 = 1.0$ where, $G_{e^-_{aq}} = 2.8$, represents the yield for production of e^-_{aq} by γ rays in the radiation-induced step 1 (10). This production of H atoms with G = 1.0 accounts for the relatively high hydrogen yields observed in the γ radiolysis of neutron solutions of glycine.[4] The limiting ammonia yield from glycylglycine in the presence of excess formate ion corresponds to $G(NH_3) = 2.5$ and we conclude in this case that the reaction of e^-_{aq} with the glycylglycine zwitterion via reaction 2a is essentially quantitative. The yield for conversion of e^-_{aq} to H by glycylglycine through reaction 2b is given by $G_{e^-_{aq}}$ to H by glycylglycine through reaction (2b) is given by $G_{e^-_{aq}} - 2.5 \leq 0.3$. Confirmation of the above formulation is found in the data of Fig. 4 which shows the effect of a competing electron scavenger, chloracetate ion (reaction 10) on ammonia yields from oxygen-free 0.25 M glycylglycine. The ammonia yield drops rapidly with increasing chloracetate concentration and the decrease in $G(NH_3)$ is accompanied by a corresponding stoichiometric increase in $G(Cl^-)$.

The formate technique has been used to measure the yield of reductive deamination in the γ radiolysis of a number of amino acids and amino acid derivatives in neutral oxygen-free solution. The results are summarized in Table II. We note first that of the compounds studied, only those with an amino group at the carbon position α to a carboxyl, ester, or peptide linkage undergo reductive deamination as a major reaction. Certainly the implication here is that the unsaturated C=O group which is common to all of the above three types of linkage is somehow involved in the deamination reaction; this aspect of the subject is treated in a later section.

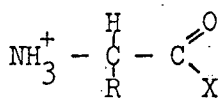
We note also from Table II that it is only with glycine and alanine that we observe a marked decrease in $\Delta G(NH_3)$ on addition of the radical scavenger. As we have noted, the reactions of OH and H radicals with these

simplest amino acids occur almost exclusively at the α-carbon position to yield radicals of the type $NH_3^{+\cdot}CR_2$. These α-carbon radicals have the property of disproportioning via reactions 6-8 to yield ammonia and carbonyl. On the other hand, the more complex amino acids, valine, for example (Table II) offer competing loci for OH and H attack at the β, γ, ν etc., positions of the side chain. Radicals formed at these sites have the chemical properties of ordinary aliphatic radicals and undergo simple dimerization without the involvement of nitrogen chemistry. Hence, the quenching of these latter reactions by formate ion does not influence $G(NH_3)$ to as great an extent. The production of diamino acids through combination of radicals formed by radical attack at β, γ, ν side-chain positions of the more complex α-amino acids has been observed by Kopoldova, Liebster, and Babicky (16).

Similarly, the presence of high concentrations of formate ion has but a relatively small effect on $G(NH_3)$ from glycylglycine, glycylglycylglycine, and glycine ethyl ester. In these cases, also, additional loci are available for OH attack and the evidence is that such attack at the terminal carbon position to give the $NH_3^{+\cdot}CR_2$ type radical is relatively unimportant. We have shown elsewhere (17) that peptides are susceptible to OH attack along the main chain to give radicals of the type $RCONH\dot{C}R_2$ which species undergo simple dimerization[5] to yield the α,α diamino acid derivatives. The present evidence is that reaction of OH with these simple peptide derivatives of glycine occurs preferentially at the C—H bond α to the peptide nitrogen.

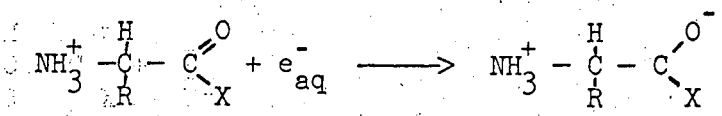
Mechanism of Reaction of e^-_{aq} with Amino Compounds

We conclude from the present study that reductive deamination via reaction 2a is a general and characteristic reaction of compounds containing the grouping



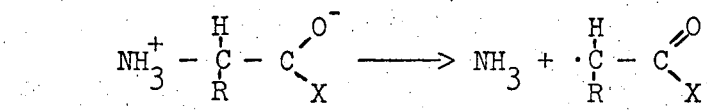
when X represents O^-, OH, OR, NHR, etc.[6] If there is more than one carbon unit between the amino and carbonyl groups reductive deamination does not occur, β-alanine and ε-aminocaproic acid are examples of amino compounds that do not undergo reductive deamination. Now, Riesz and Morris (19) found that the simple aliphatic amine cations, methyl ammonium ion, for example, react with e^-_{aq} exclusively via the conversion reaction 2b to yield H. Such reaction is analogous to the conversion of e^-_{aq} to H by NH_4^+ as observed by Jortner, et al. (20) who also showed that the rates of conversion of e^-_{aq} to H by proton donors correlate to a first approximation with the pK values of the donor acids as implied by the Brönsted general acid catalysis law. (The lower the pK the faster the reaction with e^-_{aq}.) And, Braams (13) more recently has studied, by the method of pulse radiolysis, the rate of disappearance of e^-_{aq} in oxygen-free neutral solutions of a variety of simple amines, β-amino acids, α-amino acids and peptides; he finds in all cases a reasonably good correlation between the dissociation constants of the protonated amino groups and their rate constants for reaction with e^-_{aq}. Braams concludes without specifying the nature of the chemistry involved that the protonated amino group of all of these various classes of amino compounds represents the locus of the reaction with e^-_{aq}. It is likely that such is the case for those compounds

that react with e^-_{aq} via the conversion reaction 2b in accord with the earlier work of Jortner, et al. (20). It is not clear that the same correlation between pK and reaction rate in the reductive deamination reactions of the α-amino acids, and their ester and peptide derivatives necessarily implies that e^-_{aq} is reacting at the locus of the amino group. In fact, the finding that an unsaturated double bond must be present α to the amino group for reductive deamination to occur, suggests the possibility that e^-_{aq} adds via



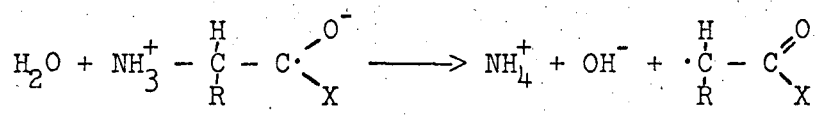
(17)

which step is then followed by the dissociation



(18)

or the hydrolysis



The recent finding that the glycine-Cu^{+2} chelate undergoes reductive cleavage of the N–C bond on reaction with e^-_{aq} as given by the overall stoichiometry (21)

$$e^-_{aq} + [Cu^{+2}(NH_2CH_2CO_2^-)_2] + H_2O \longrightarrow [Cu^{+2}(NH_3)(NH_2CH_2CO_2^-)] + OH^- + CH_2COO^- \quad (19)$$

is also consistent with the interpretation that e^-_{aq} reacts at the C=O bond of the ligand. The formulation 17, 18 is in accord with the finding that the

rate of reaction of e^-_{aq} with the zwitterion form of the α-amino acids is quite low as compared with its rate of reaction with the cation, ester and peptide forms (Table I) since the double bond character of the C=O group of the carboxylate ion is considerably less than that of the C=O group of the acid, ester, and peptide derivatives. While it is true that the rate of reaction of e^-_{aq} with the isolated peptide linkage, N-ethylacetamide, for example, is low (Table I), the presence of the NH_3^+ group in the α-position induces a strong polarization in the C=O bond (22) which would account for the enhanced reactivity of the α-amino acids towards e^-_{aq}. And, since this polarization is manifested in turn as an increase in the acid strength of the NH_3^+ group (22, 23) a correlation between the pK of the amine group and the rate of reaction of e^-_{aq} via paths 17, 18 would be expected.

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FOOTNOTES

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

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3. Some dimerization of $NH_3^{+}\dot{C}R_2$ radicals does occur but the yield of the α, α diamino acid is low (see Ref. 6).

4. For γ rays the yields of H and H_2 in the radiation decomposition of water, reaction 1 corresponds to $G_H = 0.45$, $G_{H_2} = 0.55$. With neutral 1 M glycine under γ rays $G(H_2) = 2.2$ which value is in good agreement with $G_H + G_{H_2} + 1.0$ (Ref. 2).

5. The radicals $RCONH\dot{C}R_2$ and $NH_3^{+}\dot{C}R_2$ (or $NH_2\dot{C}R_2$) differ fundamentally in their chemistry. In oxygen-free solution the former dimerize while the latter disproportionate (see Ref. 17).

6. The recent results of Clay and Kobi (Ref. 18) indicate that e^-_{aq} reacts with benzyldimethylamine cation and with benzyltrimethyl ammonium ion to yield dimethyl amine and trimethylamine respectively. This suggests the reactive grouping in the general case corresponds to $R_2NH^{+}-C(R_2)-C\begin{smallmatrix}X\\Y\end{smallmatrix}$.

Table I

Rate Constants for Reaction of e^-_{aq} with Amino Acids and Derivatives as Measured by Competition Kinetics.[a]

Compound	pH 6.7, $\bar{k}_9$ (M^{-1} sec^{-1})	pH 3, k_9 (M^{-1} sec^{-1})
glycine	1.4×10^7 (0.9×10^7)[b,c]	4.5×10^8
alanine	1.8×10^7 (0.6×10^7)[b,c]	8.0×10^8
bis-glycinato-CuII	3.5×10^8	---
glycine ethyl ester	1.0×10^9	---
diglycine	1.0×10^8 (2.5×10^8)[b]	8.9×10^8
triglycine	7.2×10^8 (9×10^8)[b]	3.0×10^9
N-ethylacetamide	1.7×10^7	1.5×10^7
N-acetyl alanine	1.1×10^7	1.2×10^8
ethyl amine		$\sim 10^6$

[a]Based on $\bar{k}_{10} = 1.2 \times 10^9$ M^{-1} sec^{-1}, $k_{10} = 6.6 \times 10^9$ M^{-1} sec^{-1}.

[b]Pulse radiolysis, Ref. 13.

[c]Pulse radiolysis, Ref. 14.

Table II

Effect of 0.8 M Sodium Formate on $G(NH_3)$ from Oxygen-Free Solutions of Amino Acids and Derivatives at pH 7.

Compound[a]	$G(NH_3)$	
	Formate-free	1.0 M formate
alanine	4.3	2.5
glycine	4.0	1.8
glycine ethyl ester	2.7	2.6
bis-glycinato-CuII[b]	5.0	3.2
glycylglycine	3.0	2.5
valine[c]	1.8	0.8
ε-aminocaprioc acid	0.35	<0.35
β-alanine	0.75	0.45

[a]At the minimum concentration required to insure the quantitative scavenging of water decomposition-products (see Fig.).

[b]At pH 8.5.

[c]Measured at only one valine concentration, viz 0.25 M.

FIGURE CAPTIONS

Fig. 1. Typical plots of the reciprocal chloride-ion yields as a function of $(R_3N)/(RCl)$ or $(\overline{R_3N})/(\overline{RCl})$ for glycine zwitterion (△), glycine cation (▲), glycylglycine zwitterion (□), glycine ethyl ester (⊠), ethylamine (●).

Fig. 2. Effect of glycine (O) and glycylglycine (●) concentrations on ammonia yields from oxygen-free solutions, pH 6.5.

Fig. 3. Effect of formate concentrations on ammonia yields from 1.0 M glycine (O), 0.20 M glycylglycine (●), oxygen-free, pH 6.5.

Fig. 4. Effect of chloracetate concentration on ammonia (●) and chloride ion (▲) yields from 0.20 M glycylglycine, oxygen-free, pH 6.5.

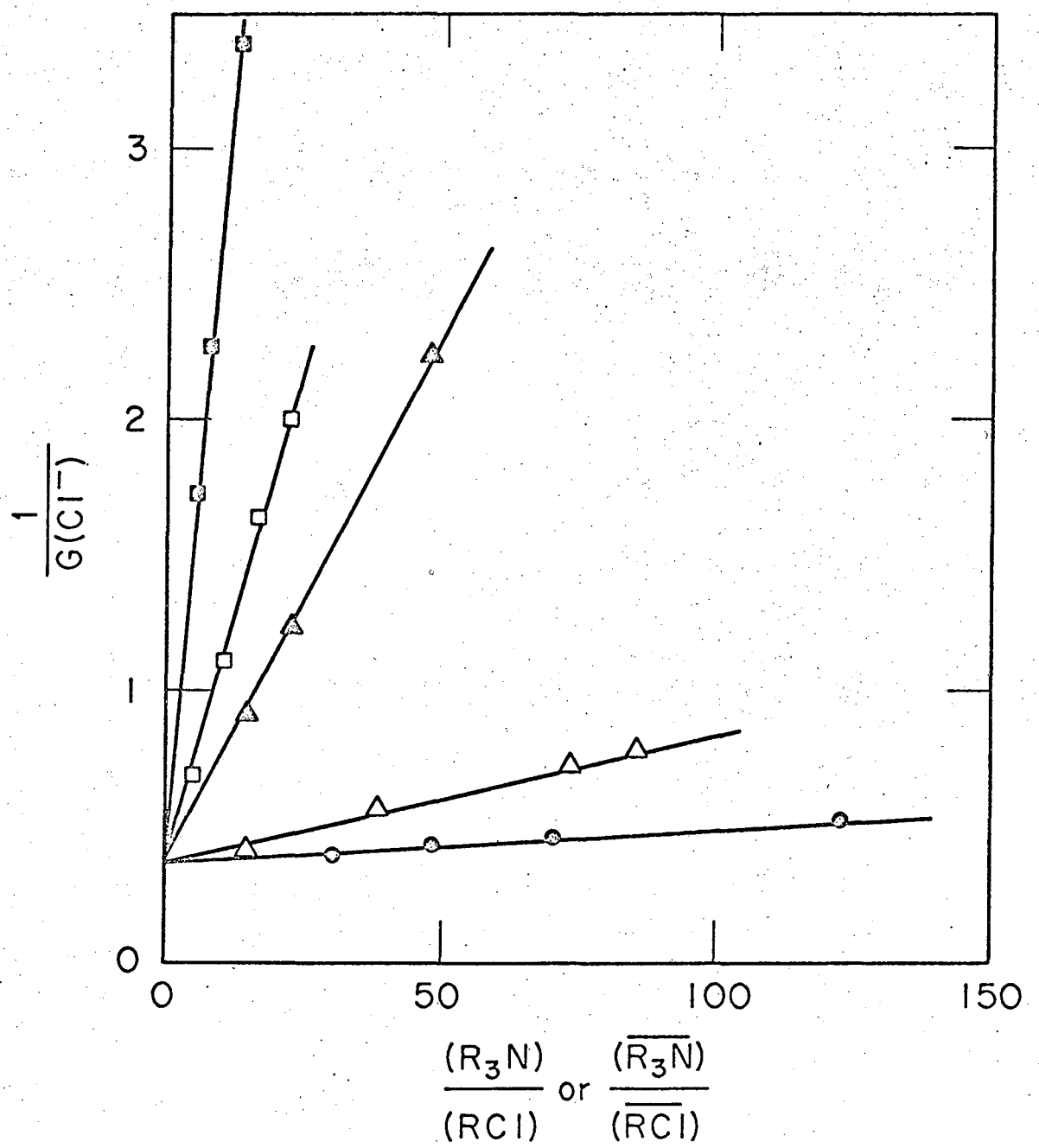

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Fig. 1

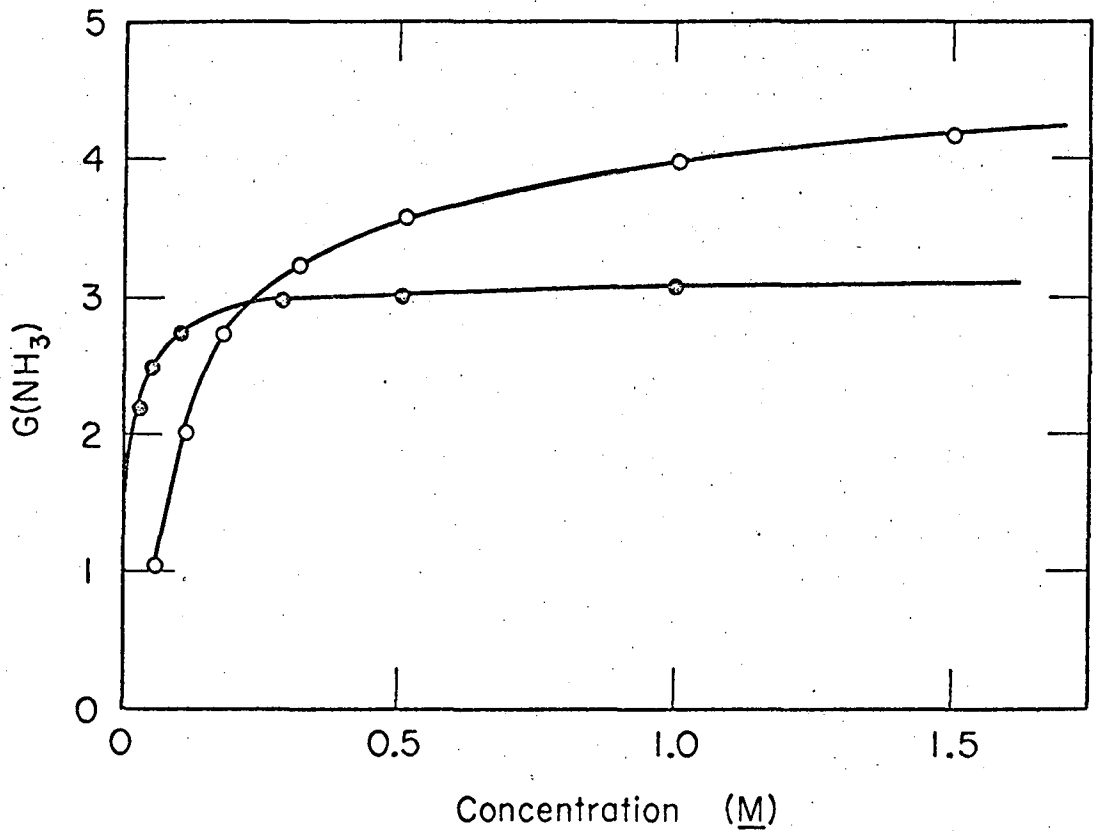

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Fig. 2

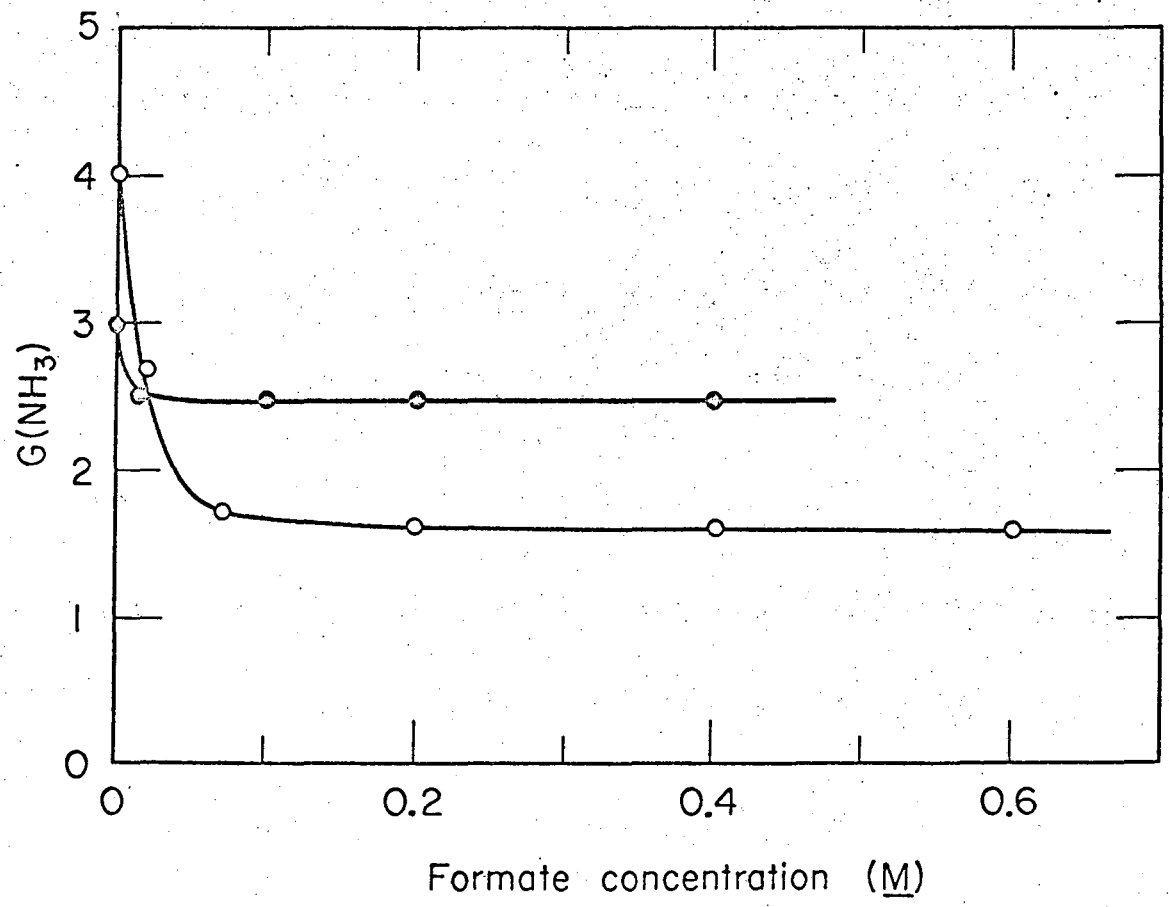

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Fig. 3

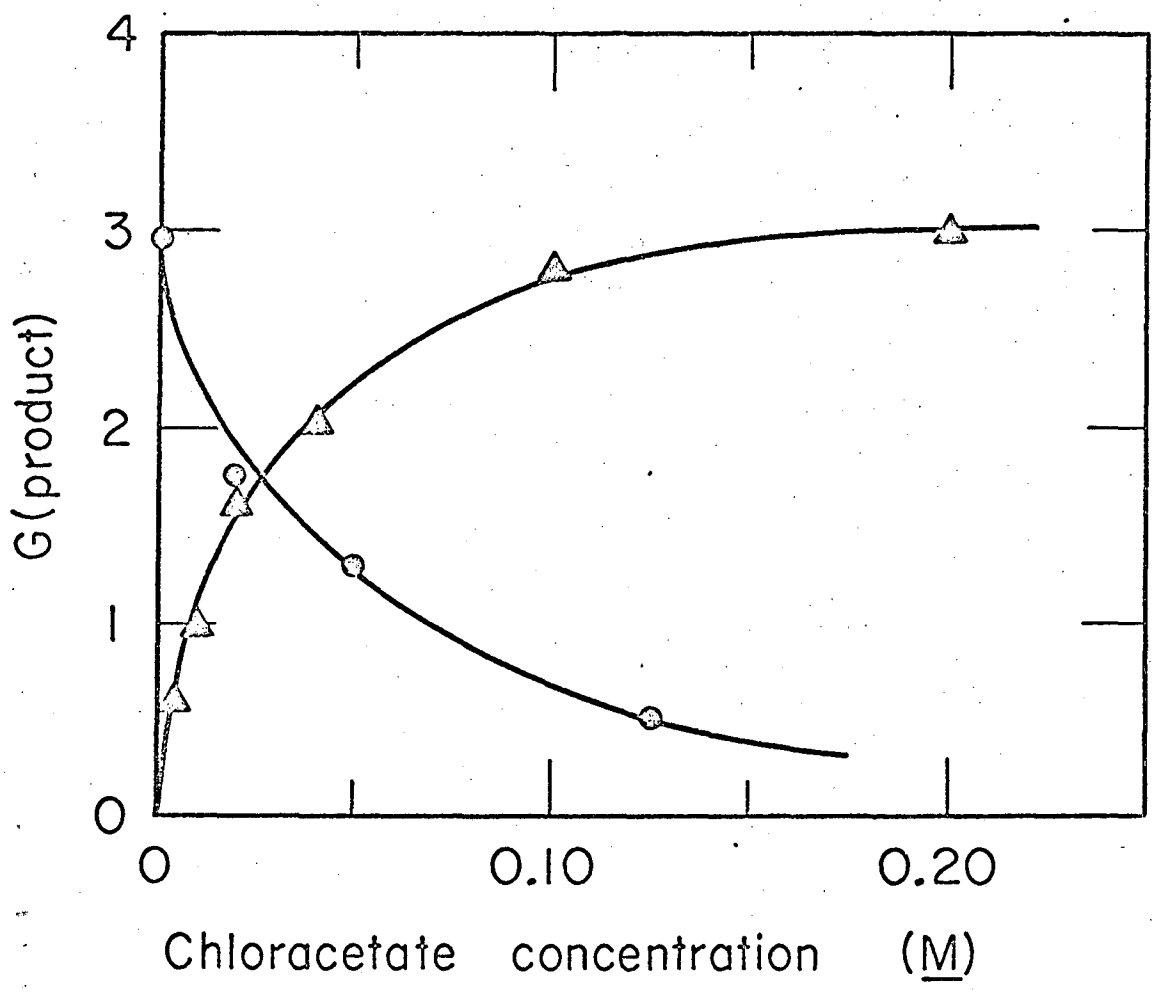

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Fig. 4

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