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REACTIONS OF ALANINE WITH THE
REDUCING SPECIES FORMED IN WATER RADIOLYSIS

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Boyd M. Weeks, Sibyl A. Cole, and Warren M. Garrison

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The principal actions of ionizing radiations on solutes in dilute aqueous solution are initiated by the radiation-induced step

$$H_2O \rightsquigarrow H_2O^+ + e^- \qquad (1)$$

which is followed within 10^{-13} sec and 10^{-11} sec respectively by the reactions

$$H_2O^+ + H_2O \longrightarrow H_3O^+ + OH \qquad (2)$$

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

where e^-_{aq} represents the hydrated electron.[2] The course of subsequent reactions in irradiated aqueous solution may be strongly influenced by pH since the hydronium ion reacts rapidly with e^-_{aq} according to

$$e^-_{aq} + H_3O^+ \longrightarrow H + H_2O \qquad (4)$$

Conversion of e^-_{aq} to H is not specific to the H_3O^+ ion. Other proton donors are also effective, ammonium ion, for example, converts e^-_{aq} via [3]

$$e^-_{aq} + NH_4^+ \longrightarrow H + NH_3 \qquad (5)$$

and the analogous reaction

$$e^-_{aq} + RNH_3^+ \longrightarrow H + RNH_2 \qquad (6)$$

might be expected to be of importance in the radiolysis of aqueous solutions of organic compounds containing the $-NH_2$ function. With the amines, a dissociative cleavage of the N-C bond may also be envisaged

$$e^-_{aq} + RNH_3^+ \longrightarrow R + NH_3 \quad . \qquad (7)$$

Some preliminary evidence on the role of reaction 7 in the radiolysis of the α-amino acids in aqueous solution has been described.[4] We report here a detailed study of the reductive deamination of alanine in oxygen-free solution under γ-rays. Data on the glycine-water system have also been included for purposes of comparison.

Experimental

Materials. Alanine and glycine (Nutrional Biochemicals) were recrystalized several times from water. The C^{14}-labeled alanine and glycine ($C^{14}OOH$) were purified chromatographically on Dowex 50 (hydrogen form). Hydrochloric acid in progressively increasing concentration (0 to 4 N) was used as the eluting agent. The separated amino-acid hydrochlorides were passed through Dowex 1 (acetate form) to remove chloride ion; the acetic acid was removed under vacuum and the amino acids were then recrystallized from water. The detailed procedures have been described.[5] Water from a Barnstead still redistilled first from alkaline permanganate and then from sulfuric acid was used in the preparation of the solutions. The chloroacetic acid (Eastman) was redistilled in vacuo. All other chemicals were reagent grade and were used without further purification. The pH adjustments were made with sulfuric acid or sodium hydroxide.

Irradiations: The pyrex irradiation cells were cleaned in nitric acid-hydrogen peroxide solution and rinsed with triply-distilled water. Ten-ml samples were irradiated in cylindrical pyrex cells with a total volume of ~40 ml. The samples containing C^{14}-labeled amino acid were irradiated at a volume of 1 ml in a proportionately smaller cell. Samples were de-gassed by evacuation. The irradiations were made with CO^{60} γ-rays from a 200 curie source. The dose-rate, $\sim 5 \times 10^{16}$ eV gm^{-1} min^{-1} over the period of this study was determined by the Fricke dosimeter, $G(Fe^{+3}) = 15.5$, $\epsilon_{305} = 2180$ at 24° C. Energy deposition in solutions was taken to be proportional to the electron density.

Analytical procedures: Gaseous products volatile at -80° C were transferred to a gas buret by means of a Toepler pump. After the total volume was measured a sample was withdrawn for mass spectrometric analysis. The system was designed so that the neutral and alkaline samples could be acdified to pH < 1 to insure quantitative recovery of carbon dioxide.

The Conway diffusion method[6] was used to separate ammonia from the irradiated solutions. The diffusates were assayed by means of the Nessler reagent. Pyruvic acid and acetaldehyde from alanine and glyoxylic acid and formaldehyde from glycine were identified by paper chromatography of the 2,4-dinitrophenyl hydrazones;[5] their separate amounts were quantitatively determined by the method of Johnson and Scholes.[7] The appropriate "blank" and control runs were made. Ammonia and carbonyl measurements were reproducible to within 5 percent.

The fatty-acid yields were determined radiometrically. Solutions containing the C^{14}-labeled amino acids at a known specific activity were irradiated and then "spiked" with measured amounts of propionic and acrylic acid in the case of alanine and acetic acid in the case of glycine. The entire sample was then placed on a silicic acid column and chromatographed with the butanol-chloroform solvent system after the method of Marvel and Rands[5,8] to separate the fatty acids from

the amino acid and from other products; propionic and acrylic acids are eluted together in a single peak. To separately determine these acids it was necessary to brominate the mixture and re-chromatograph. The mono and dibromopropionic acids are well separated from propionic acid. Yields were calculated from the specific activities of the initial amino acid solution and the isolated fatty acid.

Results

We find, in agreement with Maxwell and co-workers[9] that the major degradation products from unbuffered alanine solutions (pH6.4) include ammonia, propionic acid, pyruvic acid and acetaldehyde. In addition we find acrylic acid: the observed yield of this product varies considerably from one run to the next but averages about 10 percent of the propionic yield. Product yields from alanine increase rapidly with increasing solute concentration up to ~0.3 M and then tend toward limiting values in the concentration range ~0.5 M to ~1 M (Fig. 1). Glycine at pH 6.4 gives a very similar $G(NH_3)$- concentration plot.[10]

Figure 2 shows the marked effect of pH on the $G(NH_3)$- concentration plot for alanine. The ammonia yield is consistently about one unit greater at pH 2.8 than it is at pH 6.4 or at pH ~0.3 for alanine concentrations above about 0.2 M.

The effects of an added radical scavenger, formate ion, on $G(NH_3)$ from neutral 1 M solutions of alanine and glycine are shown in Fig. 3. The ammonia yields from both the alanine and glycine systems drop sharply with increasing concentrations of formate and then approach steady values at formate concentrations in the range 0.1 to 0.25 M. The limiting ammonia yields extrapolated to zero formate concentration correspond to $G(NH_3) = 2.5$ for alanine and $G(NH_3) = 1.6$ for glycine. The effects of 0.25 M sodium formate on the yields of fatty acids and carbonyl products from alanine and glycine, 1M, pH 6.4 are summarized in Table I. If there is any effect at all of added formate on G(propionic) and

G(acetic) it is to increase the yields by a small amount. At the same time we find that the production of carbonyl products is almost completely quenched by formate ion at 0.25 M. Table I also shows that addition of increasing amounts of chloroacetic acid to the 1 M alanine—0.25 M formate system leads to a sharp decrease in the yield of propionic acid; at 0.15 M chloroacetic acid, G(propionic) is essentially zero.

Deamination yields in 1 M alanine in the presence and in the absence of formate scavenger, 0.25 M, are given in Fig. 4 as a function of pH over the range pH 6.4 down to pH 0.3. Both curves show a maximum in $G(NH_3)$ at pH ~2 and it is also at this pH that the difference between the $G(NH_3)$ values for the two conditions is at a maximum. Note also that the slope of the $G(NH_3)$ - pH curve below pH ~2 is greater in the absence of formate scavenger. That the effect of 0.25 M formate is maximal over the entire pH range studied is shown by the data of Fig. 5, $G(NH_3)$ decreases sharply with increasing formate at pH 0.3, pH 2.8 as well as at pH 6.4 and in all cases approaches a steady value at formate concentration above 0.25 M. The yield of pyruvic acid plus acetaldehyde is decreased to $G < 0.1$ by 0.25 M formate over the whole pH range studied.

Propionic acid production over the pH range 6.4 to 0.3 in 1 M alanine and in 0.1 M alanine solutions is plotted in Fig. 6. Note that the form of the G(propionic) - pH plot for 1 M alanine has essentially the same form as the $G(NH_3)$ - pH plot for 1 M alanine—0.25 M formate (Fig. 4). Hydrogen and carbon dioxide yields for 1 M alanine over the corresponding pH range are given in Fig. 7. The hydrogen yield shows little dependence on hydrogen ion concentration at pH values > 2. The increase in $G(H_2)$ with decreasing pH below ~2 is accompanied by a decrease in both $G(NH_3)$ and G(propionic).

Discussion

We found[5] several years ago that the principal actions of ionizing radiation on the simpler amino acids such as glycine and alanine in neutral oxygen-free solution could be interpreted both quantitatively and qualitatively in terms of a reaction scheme equivalent to that given by equations 8 to 16. These reactions are written in terms of the non-ionic form of the amino acid for purposes of simplicity. The inference is that the net charge of the amino acid may influence the relative ratio but not the form of the reaction.

$$H_2O \rightsquigarrow H_2,\ H_2O_2,\ OH,\ H \qquad (8)$$

$$OH + NH_2CHROOH \longrightarrow H_2O + NH_2\dot{C}RCOOH \qquad (9)$$

$$H + NH_2CHRCOOH \longrightarrow H_2 + NH_2\dot{C}RCOOH \qquad (10)$$

$$H + NH_2CHRCOOH \longrightarrow NH_3 + \dot{C}HRCOOH \qquad (11)$$
$$\longrightarrow NH_2 + CH_2RCOOH \qquad (11a)$$

$$NH_2 + NH_2CHRCOOH \longrightarrow NH_3 + NH_2\dot{C}RCOOH \qquad (12)$$

$$\dot{C}HRCOOH + NH_2\dot{C}RCOOH \longrightarrow CH_2RCOOH + NH{=}CRCOOH \qquad (13)$$
$$\longrightarrow \text{dimer} \qquad (13a)$$

$$2\ NH_2\dot{C}RCOOH \longrightarrow NH_2CHRCOOH + NH{=}CRCOOH \qquad (14)$$
$$\longrightarrow \text{dimer}$$

$$2\ \dot{C}HRCOOH \longrightarrow \text{dimer} \qquad (15)$$

$$H_2O_2 + NH_2\dot{C}RCOOH \longrightarrow NH{=}CRCOOH + H_2O + OH \qquad (16)$$

$$H_2O + NH{=}CRCOOH \longrightarrow NH_3 + RCOCOOH \quad (17)$$

$$\longrightarrow NH_3 + RCHO + CO_2 \quad (17a)$$

Since the H atom in irradiated aqueous solution is now known to be produced largely through secondary reaction of e^-_{aq} with a proton donor, our first problem here is to identify in solutions of the amino acid zwitterions the nature of the reactions of e^-_{aq} that are the stoichiometric equivalents of the H-atom reactions given in the above reactions scheme. In the present study we assume for the γ-ray decomposition of neutral water

$$H_2O \rightsquigarrow H_2,\ H_2O_2,\ OH,\ H, e^-_{aq},\ H^+ \quad (18)$$

the 100 eV yields:[11] $G_{H_2} = 0.45$, $G_{H_2O_2} = 0.7$, $G_{OH} = 2.9$, $G_H = 0.55$, $G_{e^-_{aq}} = 2.8$.

Now, if the NH_3^+ group of the zwitterion reacts with e^-_{aq} simply as a proton donor to yield H, then, addition of a second solute known to be an effective scavenger of H (and OH) radicals would be expected to lead to a pronounced decrease in $G(NH_3)$ and G(RCHOCOOH) with increasing scavenger concentration. Formate ion is useful in this regard since it reacts rapidly with H and OH

$$H + HCOO^- \longrightarrow H_2 + COO^- \quad (19)$$

$$OH + HCOO^- \longrightarrow H_2O + COO^- \quad (20)$$

($k_{19} = 2 \times 10^8\ M^{-1}\ sec^{-1}$, $k_{20} = 10^9\ M^{-1}\ sec^{-1}$) and relatively slowly with e^-_{aq}

$$e^-_{aq} + HCOO^- \longrightarrow HCO_2^{-2} \quad (21)$$

($k_{21} < 10^5\ M^{-1}\ sec^{-1}$).[12] We find experimentally that 0.25 M formate quenches the formation of ketoacid and aldehyde from both glycine and alanine in neutral 1 M solution (Table I) and it is clear that in the presence of adequate formate scavenger there is no net oxidation of these amino acids via reactions 9 and 10. At sufficiently high concentrations of formate ion we may assume that both H and OH are preferentially removed through reactions 19 and 20 respectively and that the COO^- radicals so formed are ineffective in initiating oxidative deamination. The production of fatty acid and ammonia in the presence of excess formate (Table 1, Fig. 3) is then assigned to reactions of e^-_{aq} with the amino acid zwitterion e.g.,

$$e^-_{aq} + NH_3^+CHRCOO^- \longrightarrow NH_3 + \dot{C}HRCOO^- \qquad (22)$$

$$e^-_{aq} + NH_3^+CHRCOO^- \longrightarrow NH_2 + CH_2RCOO^- \qquad (22a)$$

This assignment is also substantiated by the observation that chloracetic acid at a concentration of 0.1 M effectively blocks the production of the fatty acid (Table I); organic chlorides are extremely reactive towards e^-_{aq}

$$e^-_{aq} + RCl \longrightarrow R + Cl^- \qquad (23)$$

($k_{23} \simeq 10^{10}\ M^{-1}\ sec^{-1}$).[12, 13]

In 1 M solutions of the glycine zwitterion, the yield for removal of e^-_{aq} through reaction 22, 22a is given by $G(NH_3) \simeq G(CH_3COOH) \simeq 1.6$ as indicated by the data of Fig. 3 and Table I. We suggest in the case of the glycine zwitterion that reaction 22, 22a occurs in parallel with the conversion reaction

$$e^-_{aq} + NH_3^+CH_2COO^- \longrightarrow H + NH_2CH_2COO^- \qquad (22b)$$

and that the yield of reaction 22b in neutral 1 M glycine is given by $G_{e^-_{aq}} - 1.6 \simeq 1.2$. Reaction 22b does not lead to glycine deamination in the presence of formate by virtue of reaction 19, but, in the absence of formate the combined yield of H atoms available for reaction 10 becomes $G_H + 1.2 \simeq 1.7$ to give $G(H_2) \simeq G_{H_2} + 1.7 \simeq 2.2$. which is close to the experimentally observed hydrogen yield from neutral 1 M glycine under γ-rays.[14] If now we substitute reactions 22 and 22a in the original reaction scheme we retain the good agreement between calculated and observed yields reported earlier.[4,5]

In the radiolysis of 1 M alanine, pH 6.4, the ammonia yield levels off at $G(NH_3) \simeq 2.5$ with increasing formate concentration (Fig. 3) and as with glycine the carbonyl yield goes to zero while the fatty acid yield remains constant (Table I). We conclude that the alanine zwitterion reacts with e^-_{aq} almost exclusively via reactions 22, 22a which are followed in the presence of formate by

$$NH_2 + HCOOH \longrightarrow NH_3 + COOH \qquad (24)$$

$$CH_3\dot{C}HCOOH + COOH \longrightarrow CH_2{=}CHCOOH + HCOOH \qquad (25)$$

$$\longrightarrow CH_3CH(COOH)_2 \qquad (25a)$$

The yield of reaction 22a is given by $G(CH_3CH_2COOH) \simeq 1.0$. Reactions 22 and 25 account for the production of acrylic acid and, since the yield of higher molecular weight acids (reaction 25a) is negligible, the yield of acrylic acid should approximate $G_{e^-_{aq}} - 1.0 \simeq 1.8$. That the observed yield is only a fraction of this is not surprising in view of the efficiency of the radical-induced chain polymerization of vinyl compounds in dilute aqueous solution.[15] Substitution of reactions 22, 22a for the H-atom reactions 11, 11a leads to an almost exact correspondence between

calculated and observed yields for major products formed in neutral 1 M alanine (Table II). In these calculations we make the assumption that the radical $CH_3\dot{C}HCOOH$ reacts preferentially as a reducing species in that reaction 13 in the case of alanine is taken to be of the form

$$CH_3\dot{C}HCOOH + NH_2\dot{C}(CH_3)COOH \longrightarrow CH_2{=}CHCOOH + NH_2CH(CH_3)COOH \quad (26)$$

The removal of e^-_{aq} by the zwitterion forms of glycine and alanine which as we have shown here gives rise to the chemistry of equations 22, 22a are relatively slow processes. Hart[12] has followed spectrophotometrically the disappearance of e^-_{aq} in neutral solutions of glycine and alanine and finds that both these solutes react with e^-_{aq} with a bimolecular rate constant of $\sim 7 \times 10^7\ M^{-1}\ sec^{-1}$; and, Maxwell[16] finds from competition studies with NO_3^- ion, a rate constant of $\sim 2 \times 10^7\ M^{-1}\ sec^{-1}$ for the reaction of e^-_{aq} with glycine in neutral solution. Since these rates are only 10^{-3} that for the reaction of e^-_{aq} with H_3O^+ ($k = 2 \times 10^{10}\ M^{-1}\ sec^{-1}$) and since, for example, in the case of alanine

$$NH_2CH(CH_3)COO^- + H^+ \rightleftharpoons NH_3^+CH(CH_3)COOH \quad K = 2.2 \times 10^2$$

it follows that the probability of capture of e^-_{aq} by the alanine zwitterion decreases rapidly with decreasing pH. However, since formate effectively quenches the oxidative deamination of alanine over the entire pH range ~ 7 to ~ 0.3 it is apparent that the e^-_{aq} also reacts with the cation and more rapidly than with the zwitterion. By analogy with reactions 22, 22a we write

$$e^-_{aq} + NH_3^+CH(CH_3)COOH \longrightarrow NH_3 + CH_3\dot{C}HCOOH \quad (27)$$
$$\longrightarrow NH_2 + CH_3CH_2COOH \quad (27a)$$

with the understanding that the relative yields of the branching reactions 22, 22a and 27, 27a are not necessarily in the same ratio. The magnitude of $G(NH_3)$ from 1 M alanine—0.25 M formate at the lower pH values (Fig. 4) shows that the reactivities of $NH_3^+CH(CH_3)COOH$ and of H_3O^+ toward e^-_{aq} are within the same order of magnitude.[17] And, although the present study was not designed to give quantitative rate data, we estimate very roughly from the initial slope of the pH-yield curve for propionic acid production in 0.1 M alanine (Fig. 6) that $k_{27}/k_4 \sim 0.2$. Maxwell[16] also has recently found that glycine in the cation form is $\sim 10^2$ times more reactive than the zwitterion toward e^-_{aq}.

We also note in regard to the capture of e^-_{aq} by the alanine cation that the addition of increasing amounts of formate scaverger to 1 M alanine at pH ~2 decreases the ammonia yield from $G(NH_3) \simeq 5.4$ to $G(NH_3) \simeq 3.5$ (Fig. 45) which value is significantly greater than that anticipated from reaction 27, 27a on the basis of $G_{e^-_{aq}} = 2.8$. And, in the absence of formate the yields of all products from 1 M alanine at pH 2 to 3 are greater [9] than we can account for in terms of the accepted yields for the decomposition of neutral water via reaction.[18] Now, Platzman[18] has pointed out that subexcitation electrons, i.e., secondary electrons with kinetic energies below that corresponding to the lowest excitation potential of water, can be effective in the direct excitation of solute species in the decimolar concentration range. And, it is not unreasonable to suggest that the chemical effectiveness of such excitation of the α-amino acids might depend on the ionic form of the solute. However, we know from other studies that the direct excitation of alanine and other amino acids by ionizing radiation[9,19] and also by ultraviolet light[20] leads to modes of decomposition that yield carbon dioxide as a major decomposition product. Since we find that $G(CO_2)$ for 1 M alanine is essentially constant from pH 6.4 down to pH 0.3 (Fig. 7) our conclusion is that the enhanced yield for alanine decomposition in acid solution is not the result of subexcitation-electron effects. We note, however, that there is accumulating

evidence[21] that as the pH of a solution is reduced below 3 to 4 the yield for water decomposition actually increases presumably as a result of the stoichiometry[21b]

$$H_2O^* + H^+ \longrightarrow H_2^+ + OH \qquad (28)$$
$$H_2^+ \longrightarrow H + H^+$$

where H_2O^* represents either an excited water molecule or an isolated radical pair (H, OH) which species revert to water at pH > 4 by first order kinetics. It is clear, however, that scavenging of H_2O^* by H^+ to yield additional H and OH cannot be responsible for the enhancement with decreasing pH of product yields from 1 M alanine containing excess formate scavenger. On the other hand, the present experimental requirements appear to be wholly satisfied by a reductive deamination of the amino acid cation by H_2O^* via the stoichiometry

$$H_2O^* + NH_3^+CHRCOOH \longrightarrow NH_4^+ + R\dot{C}HCOOH + OH \qquad (29)$$
$$\longrightarrow NH_3^+ + RCH_2COOH + OH \qquad (29a)$$

where $G_{H_2O^*} \cong 0.8$ and where the radical products of reactions 29, 29a are subsequently removed through steps 9, 12, 26.

As the pH is decreased below ~2 the hydrogen yield begins to increase as a consequence of the competition of H_3O^+ for reducing species according to reactions 4 and 28. The present data do not provide a basis for estimating the relative importance of reactions 4 and 28 in the production of the additional hydrogen.

From the radiation chemistry reported here thus far one might assume that reduction cleavage of the N-C bond represents a characteristic radiation chemical property of amines generally. However Riesz[22] finds no evidence for such reaction in the radiolysis of oxygen-free solutions of the methyl ammonium ion nor do we find any important contribution of reductive deamination in our

preliminary studies of the effects of H and OH scavengers on the radiation chemistry of β-alanine. The α-amino acids appear to represent a special case and we can only speculate at the present time on the role of α-substitution in the reductive cleavage of the N-C bond by e^-_{aq}. One possibility of course is that e^-_{aq} interacts with the π-electrons of the C=O group and that dissociation of the N-C bond at the α position occurs on rearrangement of the intermediate complex. It would appear that further consideration of these reactions must await additional information on the radiation chemistry of the variously substituted amines.

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FOOTNOTES AND REFERENCES

1. This work was done under the auspices of the U. S. Atomic Energy Commission.

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17. Although HCOOH is considerably more reactive towards e^-_{aq} than is $HCOO^-$ (ref. 12) this solute still acts preferentially as a scavenger of H and OH in acidic 1 M alanine because of the increased reactivity of the cation form toward e^-_{aq}.

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Table I

Effect of scavengers on the yields of organic products from solutions of alanine and glycine at pH 6.4.

	[formate]	G		
		fatty acid	keto acid	aldehyde
1.0M alanine	none	1.0	1.5	0.5
1.0M alanine	0.25	1.1	<.1	<.1
1.0M glycine	none	1.7	2.3	0.6
1.0M glycine	0.25	1.8	<.1	<.1

	[chloroacetate]			
1.0M alanine	none	1.1	1.5	0.5
+	.05	.25	-	-
0.25M formate	.15	<.1	<.1	-

Table II

Observed and calculated yields of products from 1 M alanine, pH 6.4.

Product	G	
	Observed	Calculated[a]
Ammonia	4.3	4.8
Propionic acid	1.0	1.0[b]
Pyruvic acid	1.6	1.4
Acetaldehyde	0.5	0.60
Carbon dioxide	0.60	0.60[b]
Hydrogen	1.25	1.0

a. Based on the accepted yields for water decomposition (ref. 11) and the reaction scheme formulated in the present work

b. The observed yields of propionic acid and carbon dioxide give the branching ratios for reactions 22, 22a and 17, 17a respectively.

Figure Captions

Figure 1. Yields of ammonia (O), pyruvic acid (△), and acetaldehyde (▲) as a function of alanine concentration of pH 6.4.

Figure 2. Yield of ammonia as a function of alanine concentration at pH 0.3(●), pH 2.8 (◐), pH 6.4 (O).

Figure 3. Yield of ammonia from 1.0 M alanine (O) and 1.0 M glycine (●) as a junction of sodium formate concentration at pH 6.4.

Figure 4. Yield of ammonia from 1 M alanine (O) and 1.0 M alanine-0.25 M [illegible] formate (●) as a function of pH.

Figure 5. Yield of ammonia from 1 M alanine as a function of sodium formate concentration, pH 0.3 (●), pH 2 (◐), pH 3.4 (◑), pH 6.4 (O).

Figure 6. Yield of propionic acid as a function of pH in 1.0 M alanine (□) and 0.1 M alanine (■).

Figure 7. Yields of hydrogen (◇) and carbon dioxide (◆) from 1M alanine as a function of pH.

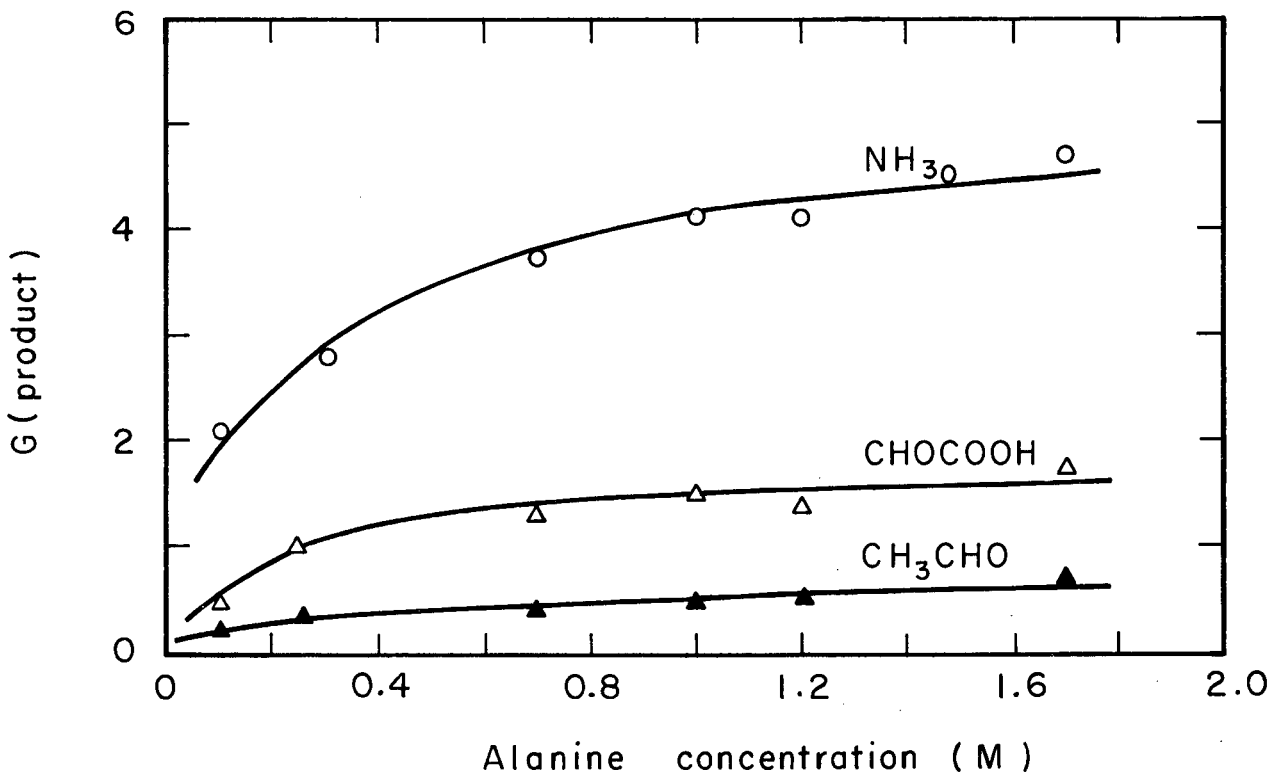

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Fig. 1

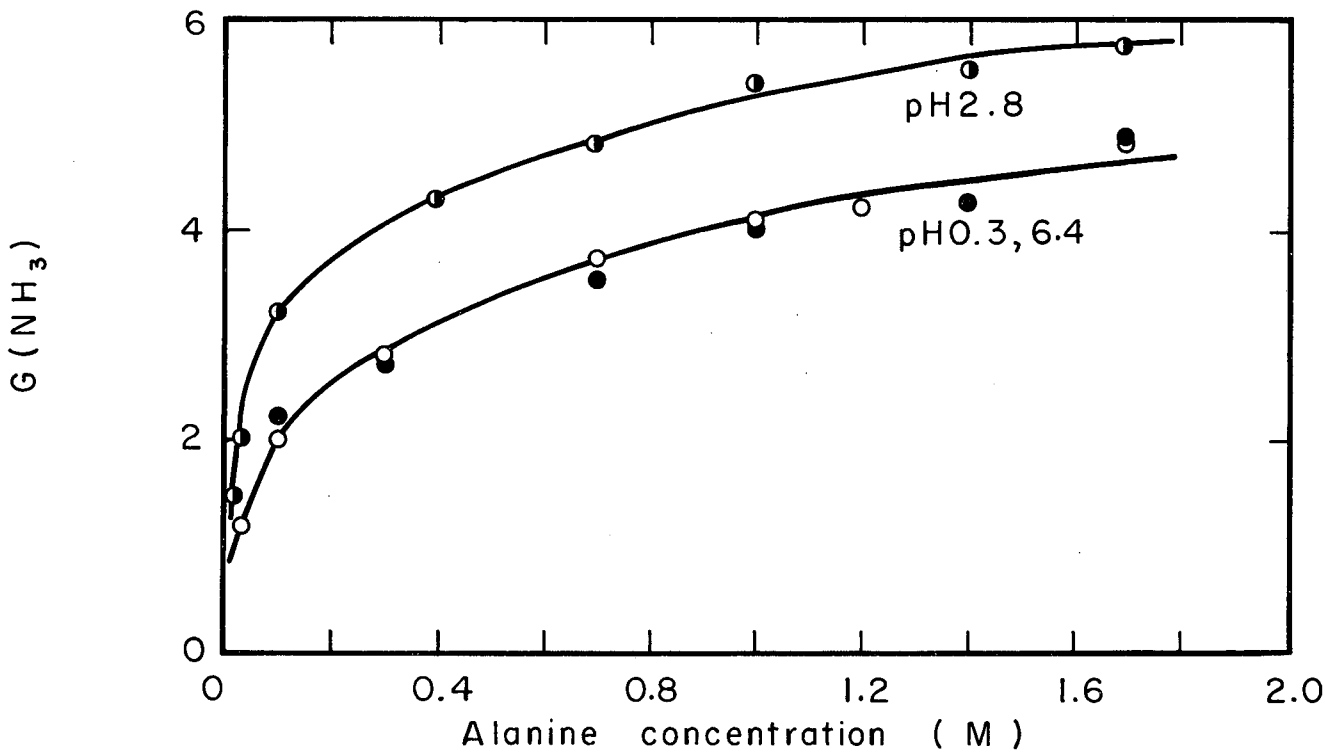

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Fig. 2

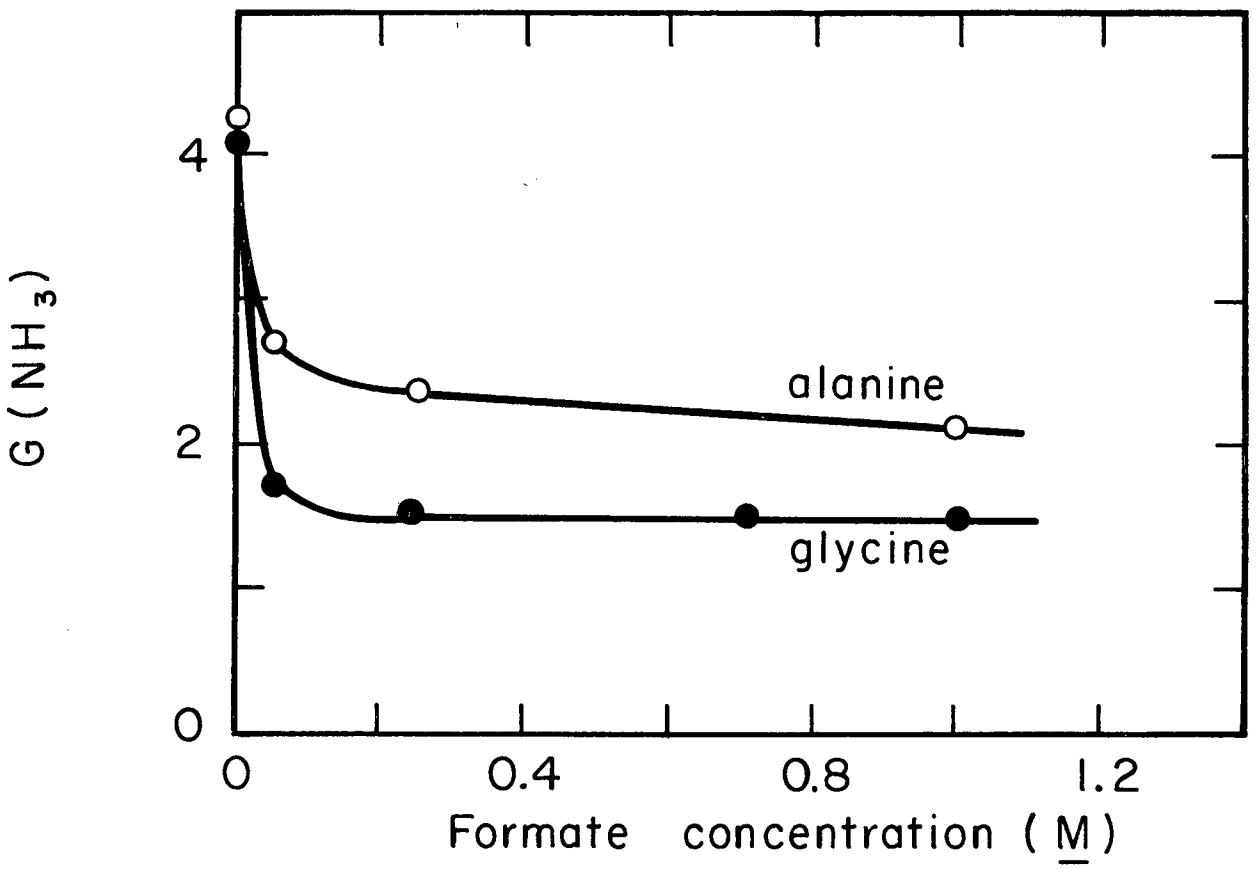

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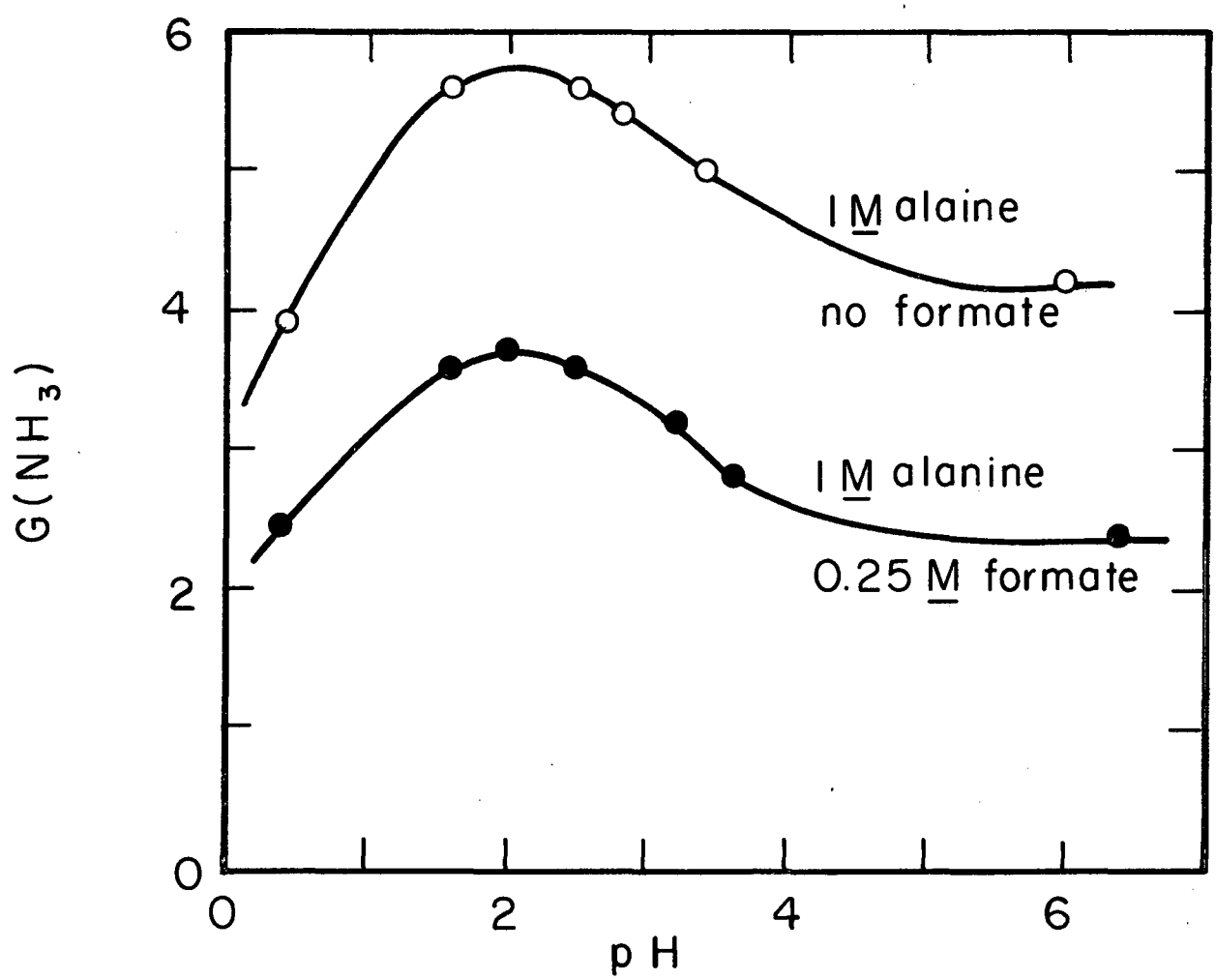
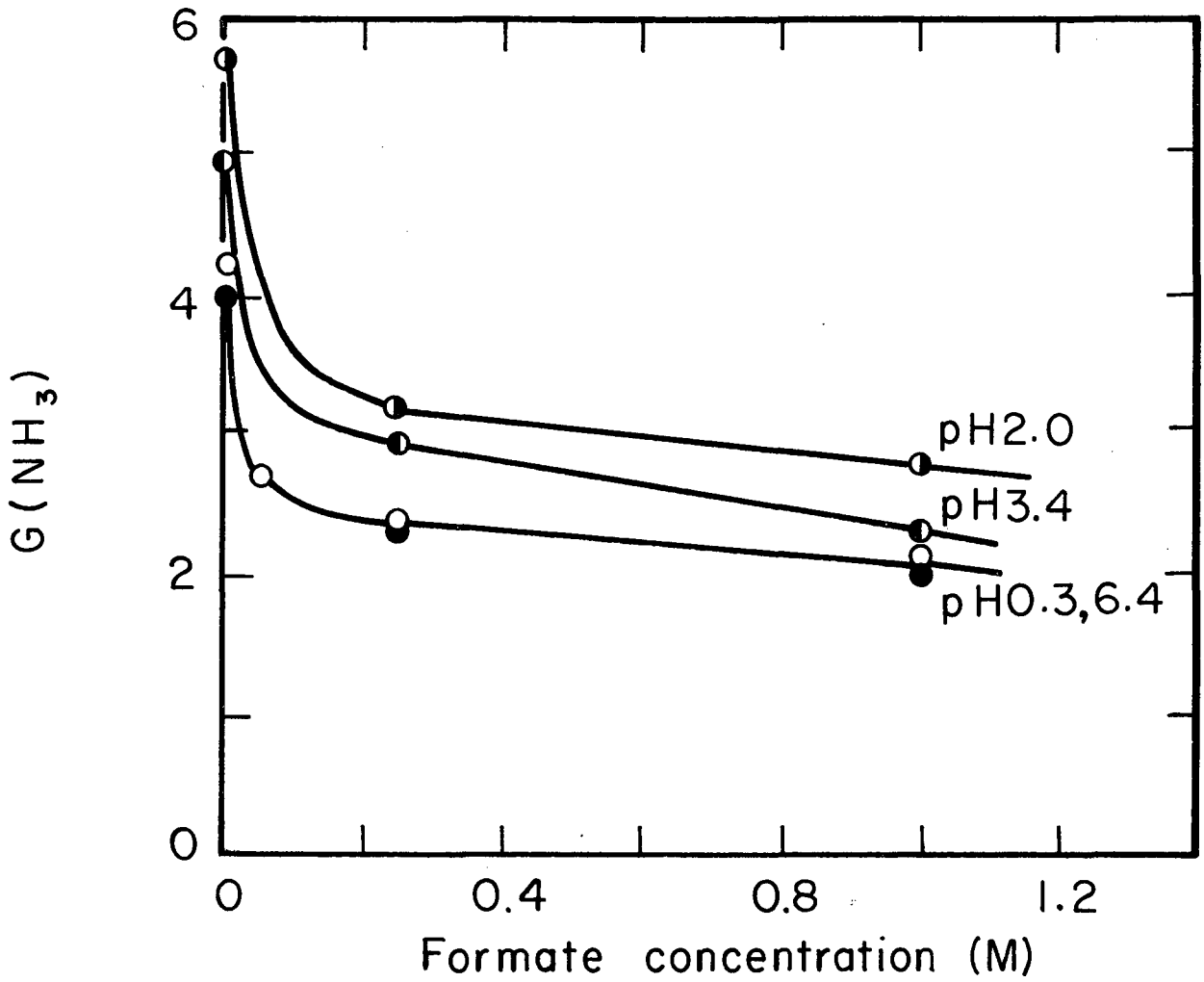
Fig. 3



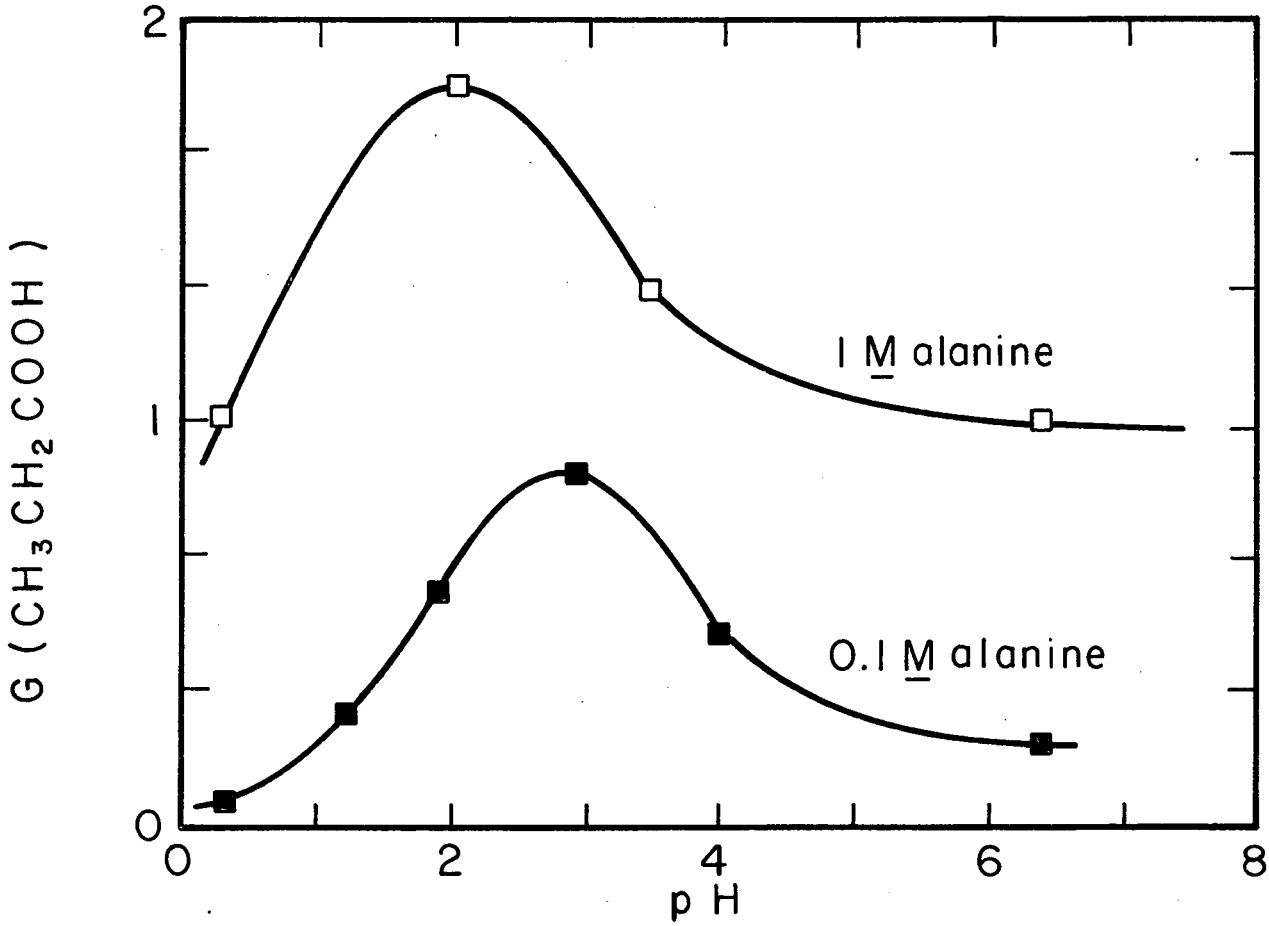
MUB-5829

Fig. 4



MUB-5830

Fig. 5



MUB-5831

Fig. 6

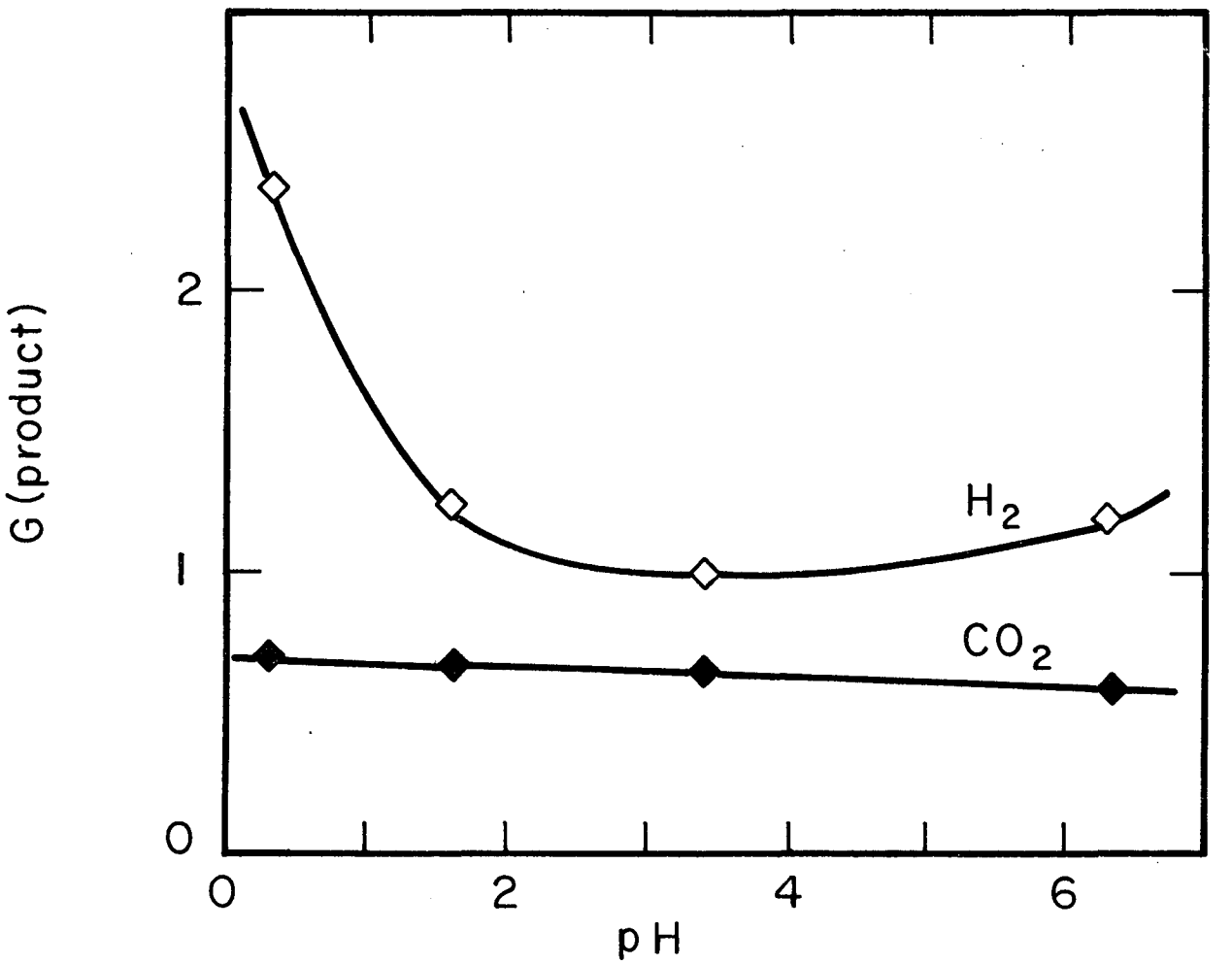


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Fig. 7

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