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IONIZATION AND EXCITATION IN PEPTIDE RADIOLYSIS

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November 1967

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ABSTRACT

Major chemical affects of γ-rays on simple peptides in the polycrystalline state, in the glassy state and in concentrated aqueous solutions lead to degradation of the peptide chain. Several different reaction modes are involved and these all yield amide-like products that readily hydrolyze to give ammonia. Major concomitant products include fatty acid, ketoacid and aldehyde. Studies of N-acetylalanine glass containing added electron scavengers provide a measurement of the ionization yield, $G_{e^-} \simeq 3$. Conventional radical scavengers have relatively little effect on $G(NH_3) \simeq 3.5$. However, certain aromatic compounds effectively quench a major fraction of the (amide) ammonia yield. The evidence is that ketoacid and aldehyde are formed from positive-ion intermediates while fatty acid and amide are derived through reactions involving excited (triplet) states.

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I. INTRODUCTION

A major chemical effect of γ-rays on simple peptides such as the N-acylamino acids under oxygen-free conditions, both in the solid state and in concentrated aqueous solution, leads to formation of labile amide-like compounds which are readily degraded on mild hydrolysis to yield ammonia as a characteristic product. Several classes of nitrogen-deficient products are formed concomitantly with the ammonia. Earlier communications have discussed certain limited aspects of the radiolytic lability of simple peptides in the solid state and in concentrated solutions (9,10,18). The radiation chemistry of these systems is more complex than that involved in the radiolysis of simple peptides in dilute oxygen-free aqueous solution under which conditions main-chain degradation is of minor importance (10). In this paper we report detailed experimental evidence and specific formulations for a number of degradation modes that have been found to be induced directly through ionization and excitation of peptides in the polycrystalline state, in the glassy state, and in concentrated aqueous solution.

II. EXPERIMENTAL

A. Materials

The N-acetylamino acids were of reagent grade or of the highest purity available commercially (Cyclo Chemicals, K and K Laboratories, Mann Research Laboratories, Nutritional Biochemicals) and were recrystallized at lease once from distilled water. Polyalanine (Yeda, M. W. 1700) was dialyzed against distilled water and lyophilized. Chloracetic acid (Eastman) was redistilled *in vacuo*. Other chemicals were of C.P. grade. Water from a Barnstead still

was redistilled first from alkaline permanganate and then from phosphoric acid. The pH adjustments were made with NaOH or H_2SO_4.

1. Sample Preparation and Irradiation

To obtain acetylalanine glass, the polycrystalline free acid was dissolved to ~2M in redistilled water and the solution was adjusted to pH 6.5 with NaOH. Ten-ml aliquots were transferred to flat-bottomed cylindrical irradiation cells (2.5 cm. diam.) and water was slowly removed on the vacuum-line. The solutions were kept at 0°C during the dehydration. Under these conditions the water content gradually decreases over a period of 24 hours until a clear glass of composition $CH_3CONHCH(CH_3)COONa \cdot 2H_2O$ is obtained. Additional four to six hours pumping does not change the water mole-fraction appreciably. The samples were irradiated at 0°C. More dilute solutions were prepared in the ordinary way. The polycrystalline N-acetylamino acid RCONHCH(R)COOH, and the polyalanine were degassed by evacuation on the vacuum line for at least 24 hours prior to irradiation.

All samples were irradiated with Co^{60} γ rays at a dose-rate of 1.2×10^{18} ev/gm/min as determined by the Fricke dosimeter $\left[G(Fe^{+3}) = 15.5,\ \epsilon_{305} = 2180 \text{ at } 24°C\right]$. Energy deposition in the solids and concentrated solutions was taken to be proportional to electron density.

2. Analytical Methods

Gaseous products were pumped off following complete dissolution of the irradiated solid in degassed water on the vacuum line; analysis was by mass spectrometry (Consolidated 120) and by gas-chromatography (Aerograph A90-P3).

For other analyses, the irradiated solids were dissolved in water under nitrogen in a glove box.

Free ammonia and amide ammonia were determined by a modification of the micro-diffusion method of Conway (6); the diffusates were assayed by means of Nessler reagent. In the measurement of free ammonia, the samples were diluted three times with saturated K_2CO_3 solution in the outer compartment of the diffusion cell; recovery of ammonia in the acid compartment (0.1N H_2SO_4) is complete in three hours. For total ammonia (free plus amide) the sample was made 2N in NaOH; hydrolysis and transfer is complete in 24 hours. The necessary blank and standard runs were made in parallel.

The fatty acids were separated through lyophilization of the sample solution after acidification to 2N with H_2SO_4. Assay was by vapor-phase chromatography (Aerograph, 600C). The polyalanine was dissolved in 2N H_2SO_4 (under N_2) and hydrolyzed 18 hours prior to lyophilization.

Carbonyl products were identified by paper chromatography of the 2,4-dinitrophenylhydrazones (20). The irradiated N-acetylalanine showed only pyruvic acid and acetaldehyde. These were determined quantitatively by the method of Johnson and Scholes (13) with minor modifications. Chloride ion was determined by the method of Luce et al. (15) after Hayon and Allen (12).

A colorimetric method (8) was used to set a limit on the yield of lactic acid.

III. RESULTS AND DISCUSSION

The 100 ev yield for the radiolytic degradation of the peptide bond, as measured in terms of $G(NH_3)$ after mild hydrolysis, has been determined for a

variety of aliphatic, aromatic and sulfur-containing amino acids in the N-acetyl form. These data are summarized in Table I. In the case of the aliphatic series, we note that the length of the side-chain has relatively little effect on the yield of main-chain degradation. The effect of the aromatic groups of acetyl phenylalanine and of acetyl tyrosine is to quench in part the yields of those reactions that lead to formation of amide ammonia. The sulfur moiety of methionine on the other hand appears to be relatively ineffective in quenching such reactions.

As a preliminary step in this inquiry into the nature of the radiolytic processes that lead to degradation of the peptide chain, we have completed a detailed study of the reaction products formed in the γ-radiolysis of simple peptide derivatives of alanine, viz poly-DL-alanine and acetyl-DL-alanine polycrystalline. These data are summarized in Table II. We find that the major organic products in the order of decreasing yield are propionic acid, acetaldehyde, pyruvic acid, and lactic acid. The labile ammonia from acetylalanine, G = 3.4, is derived primarily from acetamide, G = 2.8, plus a small amount of free ammonia, G = 0.6.

The presently available data on product yields from other N-acetylamino acids is less complete although the limited data of Table III are consistent in showing for the aliphatic N-acetyl amino acids that the corresponding fatty acid represents the major nitrogen-deficient product.

From these studies of the concomitant organic products it is clear that the observed $G(NH_3)$ values represent the combined yield of a number of different modes of degradation of the peptide chain. And, before proceeding to detailed considerations of elementary processes, it is useful here to formulate

working hypotheses as to the stoichiometry of these reactions. First of all we note that the maximal yields of lactic acid and of the carbonyl products, acetaldehyde and pyruvic acid from acetylalanine are obtained only after hydrolysis of the irradiated solid. The present chemical requirements are met by the stoichiometric relationships

$$RCONHCHR_2 \longrightarrow R\overset{\overset{NH}{\|}}{C}OCHR_2 \qquad (1)$$

$$RCONHCHR_2 \longrightarrow RCON{=}CR_2 + H_2(2H) \qquad (2)$$

$$RCONHCHR_2 \longrightarrow RCON{=}CHR + RH \qquad (3)$$

The radiation-induced N-O shift represented by Eq. (1) leads to formation of a labile imino ester which species is readily hydrolyzed to yield ammonia and the hydroxyacid, lactic acid

$$R\overset{\overset{NH}{\|}}{C}OCHR_2 + H_2O \longrightarrow RCOOH + NH_3 + RCHOHR \qquad (4)$$

The unsaturated products (dehydropeptides) of Eqs. (2,3) are labile and readily hydrolyze to yield amide plus pyruvic acid and acetaldehyde respectively (11)

$$RCON{=}CR_2 + H_2O \longrightarrow RCONH_2 + R_2CO \qquad (5)$$

$$RCON{=}CHR + H_2O \longrightarrow RCONH_2 + RCHO \qquad (6)$$

Acetyl α-aminobutyric acid yields α-ketobutyric acid and propionaldehyde in accord with the above formulation.

The formation of propionic acid as the principal organic product of the radiolysis of acetylalanine implies that direct main-chain cleavage is involved as the major decomposition mode. We tentatively define the stoichiometry of this cleavage in terms of

$$RCONHCHR_2 \longrightarrow RCO\dot{N}H + \dot{C}HR_2 \tag{7}$$

$$RCO\dot{N}H + RCONHCHR_2 \longrightarrow RCONH_2 + RCONH\dot{C}R_2 \tag{8}$$

$$\dot{C}HR_2 + RCONHCHR_2 \longrightarrow CH_2R_2 + RCONH\dot{C}R_2 \tag{9}$$

where the radicals $RCONH\dot{C}R_2$ are long-lived and correspond to the radical species observed at room temperature by esr measurements (4). On dissolution in water (oxygen-free) the α-carbon radicals $RCONH\dot{C}R_2$ undergo dimerization to yield α,α'-diaminosuccinic acid derivatives (10). The formulation of Eqs. (7,8,9) is intended only to convey the nature of the overall stoichiometry. Ionic and/or excited species are presumably involved as actual intermediates since caging effects in the solid phase would lead to preferential recombination of the radical pair of Eq. (7). It is this question of the nature of the intermediates involved in the formation of amide and fatty acid that we now consider.

The initial radiation-induced step we represented in terms of the ionization

$$RCONHCHR_2 \rightsquigarrow (RCONHCHR_2)^+ + e^- \tag{10}$$

Simple charge recombination may be envisaged as leading to dissociation of the N-C bond

$$e^- + (RCONHCHR_2)^+ \longrightarrow RCO\dot{N}H^{\ddagger} + \dot{C}HR_2 \tag{11}$$

to give radicals with excess energy which would tend to favor the abstraction reactions (8,9) in competition with radical recombination. Alternatively, the ion-molecule reaction

$$(RCONHCHR_2)^+ + RCONHCHR_2 \longrightarrow RCONH_2^+CHR_2 + RCONH\dot{C}R_2 \qquad (12)$$

which is of the type observed in other polar organic systems (16,21) may occur prior to the neutralization

$$e^- + RCONH_2^+CHR_2 \longrightarrow RCONH_2 + \dot{C}HR_2 \qquad (13)$$

The other possibility of course is that the electron escapes the positive charge and reacts at a distance e.g.

$$e^- + RCONHCHR_2 \longrightarrow RCON\bar{H} + \dot{C}HR_2 \qquad (14)$$

We note that the radiation-induced step 10 followed by electron removal via anyone of the reactions (11,13,14) leads to the stoichiometry of Eqs.(7-9).

It is of interest therefore to consider at this point the effects of added electron scavengers on the yield of main-chain rupture. Fortunately, for this purpose we have been able to prepare N-acetylalanine in the form of a clear glassy solid at room temperature. The glass has the composition $CH_3CONHCH(CH_3)COONa \cdot 2H_2O$, and gives product yields that are essentially the same as those obtained with the polycrystalline solid e.g. $G(NH_3) \simeq 3.4$, G(propionic) = 1.6, G(acetaldehyde) = 0.8 Chloracetate ion which has been

shown to be an effective electron scavenger

$$e^- + RCl \longrightarrow R + Cl^- \qquad (15)$$

in other polar glasses (3) is soluble (as the sodium salt) in acetylalanine glass when prepared as described in the experimental part of this paper. We find that $G(Cl^-)$ increases with chloracetate concentration in the concentration range 1 to 10 mole percent as shown in Fig. 1; the reciprocal-yield plot of Fig. 2 gives a limiting value of $G(Cl^-) \simeq 3$ which value provides a measure of the yield for ion-pair production via reaction 10 in the present system. At the same time there is but a small effect of added chloracetate on $G(NH_3)$ even under the condition in which $G(Cl^-)$ is maximal. The evidence is then that the electron-capture reactions of type 11,13,14 do not represent major paths for cleavage of the N-C bond.

There would appear to be two remaining possibilities; (a) the positive ions formed in reaction (10) undergo fragmentation, for example

$$(RCONHCHR_2)^+ \longrightarrow RCONH^+ + \dot{C}HR_2 \qquad (16)$$

$$RCONHCHR_2 + (RCONHCHR_2)^+ \longrightarrow RCONH_2^+ + \dot{C}HR_2 + RCONH\dot{C}R_2 \qquad (16a)$$

and/or (b) neutral excited species are formed through a process other than that of charge recombination and subsequently undergo unspecified chemistry to yield amide and propionic acid. To obtain information on the possible importance of these reaction modes, we have taken advantage of the fact that the acetylalanine glass $CH_3CONHCH(CH_3)COON_a, 2H_2O$ is miscible with water in all

proportions. If direct energy-absorption in the peptide via reaction (10) followed by the dissociation reaction (16) is of importance, we would expect that the degradation yields would decrease with increasing water content of the system. The possibility that ionization in water

$$H_2O \rightsquigarrow H_2O^+ + e^- \tag{17}$$

is followed by charge transfer e.g.

$$H_2O^+ + RCONHCHR_2 \longrightarrow RCONH^+ + CHR_2 \tag{18}$$

or

$$H_2O^+ + RCONHCHR_2 \longrightarrow RCONH_2^+ + \dot{C}HR_2 + OH \tag{18a}$$

would also be excluded at the higher water concentrations by virtue of the fast competing reaction (14)

$$H_2O^+ + H_2O \longrightarrow H_3O^+ + OH. \tag{19}$$

The effects of added water on $G(NH_3)$ and G(propionic) from the sodium salt of acetylalanine are summarized in Fig. 3. The ammonia yield which as we have noted is derived from a number of reaction modes shows but a small decrease, $\Delta G(NH_3) \sim 1$, as the acetylalanine concentration is decreased to 1M. And, even more striking is the fact that the yield of the major organic product, propionic acid, is essentially independent of acetylalanine concentration over the entire range of Fig. 3. Our tentative conclusion is then that cleavage of the N-C

bond to yield propionic acid does not arise in the main from the positive-ion chemistry of reactions (16,16a,18,18a).

On lowering the acetylalanine concentration from 1M to 0.1M, G(propionic) drops to zero and $G(NH_3)$ decreases to 0.5; the chemistry of these dilute solutions is of a different nature as we have described elsewhere (10,2).

Now, we have already noted on the basis of the chloracetate data of Fig. 1, that electron capture via reactions (11,13,14) does not represent a major path for cleavage of the N-C bond in the case of the acetylalanine glass, $CH_3CONHCH(CH_3)COON_a \cdot 2H_2O$. Similarly, we find that the quantitative scavenging of e^-_{aq} by chloracetate ion in 2M acetylalanine solution has relatively little effect on $G(NH_3)$ as shown by the data of Fig. 4. And, we also observe from Fig. 4 that the preferential removal of OH radicals by formate ion has essentially no effect on $G(NH_3)$ from the 2M solution.

By a process of elimination, then, we come to a consideration of the possibility that amide formation in these concentrated peptide solutions involves reactions of neutral excited species. Now, aromatic compounds are, of course, known to be effective scavengers of excited states providing the energy levels of the excited species are higher than those of the quencher (22). We do find that certain aromatic solutes such as naphthalene sulfonic acid, benzaldehyde and benzoic acid at millimolar concentrations are remarkably effective in quenching the formation of amide ammonia in 2M acetylalanine. Typical data for naphthalene sulfonic acid are shown in Fig. 5. We also find that phenol and benzene sulfonic acid are essentially without effect even at the higher concentrations. There is, of course, the possibility that the quenching of $G(NH_3)$ by napththalene sulfonic acid, benzaldehyde and benzoic acid

involves simply the scavenging of an amide precursor via radical-addition to the benzene ring, for example

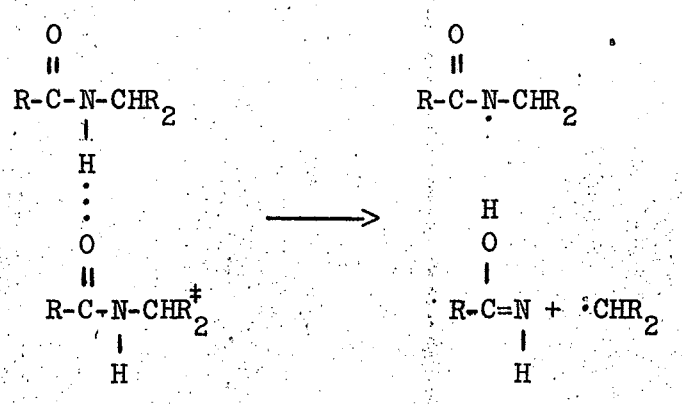
$$CH_3\dot{C}ONH + \emptyset H \longrightarrow CH_3CONH\dot{\emptyset}H \qquad (20)$$

However, if this were the case both phenol and benzene sulfonic acid should also be effective. In fact, rates for radical addition to phenol are even faster than those for addition to benzaldehyde and benzoic acid (1). We can only conclude from the present observations in toto that (a) a major fraction of the N-C fragmentation in these concentrated solutions does indeed arise from reactions of excited species and that (b) such reactions can be effectively quenched through excitation transfer to solutes such as naphthalene sulfonic acid benzaldehyde and benzoic acid. That benzene sulfonic acid and phenol are ineffective quenchers in the present system is not inconsistent with the fact that the energy levels (singlet and triplet) of these two benzene derivatives are somewhat higher than those of the effective quenchers. We note that the singlet-state levels of all of the aromatics studied here (5) are well below the singlet-state level of the peptide bond (19). Hence the fact that naphthalene sulfonic acid quenches while phenol does not would suggest we are dealing with a triplet-state of the peptide configuration. The reciprocal-yield plot of Fig. 5 gives $G(NH_3) = G(\text{propionic}) = 1.6$ as the excitation yield in 2M acetylalanine.

Excitation of the peptide bond by low-energy electrons via

$$e^- + RCONHCHR_2 \longrightarrow RCONHCHR_2^{\ddagger} + e^- \qquad (21)$$

would be consistent with the present experimental requirements. A theoretical treatment of this mode of excitation for the general case has been given by Platzman (17). We envisage the chemistry of the excited state both in concentrated solution and in the solid systems to be of the form:



(22)

where $RC\dot{O}NCHR_2$ rearranges instantaneously to give the long-lived radical $RCONH\dot{C}R_2$. Since the radical products of reaction (22) are formed at a distance, the effects of caging will be minimal. The over-all energy requirement for reaction (22) is essentially that required for dissociation of the aliphatic N-C bond i.e. ~3 ev(7).

If solid acetylalanine is irradiated at the temperature of liquid nitrogen, then the propionic acid is almost wholly quenched from $G(\text{propionic})_{290°K} = 1.6$ to $G(\text{propionic})_{77°K} \leq 0.1$. The ammonia yield shows a corresponding drop from $G(NH_3)_{290°K} = 3.2$ to $G(NH_3)_{77°K} = 1.3$. We interpret this as evidence that an energy of activation is involved in reaction (22). The yields of carbonyl products, on the other hand, are unchanged at the lower temperature with $G(\text{carbonyl})_{77°K} = G(NH_3)_{77°K} = 1.3$. We suggest that the carbonyl products arise from positive ion precursors

$$RCONHCHR_2 \longrightarrow (RCONHCHR)^+ + R + e^- \quad (23)$$

$$RCONHCHR_2 \longrightarrow (RCONHCR_2)^+ + H + e^- \quad (24)$$

which species undergo proton stripping to yield the dehydropeptide derivatives referred to in Eqs. (2,3).

We conclude, then, from these studies of elementary processes in peptide radiolysis that (a) a number of reaction modes are of importance in the radiolytic degradation of the peptide chain, (b) charge recombination does not appear to be involved as a step in any of the major reaction sequences that lead to main-chain degradation, (c) the electron escapes the positive ion and can be chemically trapped by appropriate electron scavengers, (d) positive-ion chemistry leads to the formation of carbonyl products, (e) neutral excited species appear to be major intermediates in the radiation-induced cleavage of the N-C bond to yield amide and fatty acid. Although, this is not the place to speculate on the radiation-biological implications of particulars (a) to (e), we would, nevertheless, point our that finding (e) suggests that excitation scavengers as well as radical scavengers can be of importance in mitigating the biological effects of ionizing radiations.

Table I. γ-ray induced degradation of solid N-acetylamino acids, $CH_3CONHCH(R)COOH$.

N-acetyl Derivative[a]	(R)	$G(NH_3)$[b]
glycine	-H	2.68
alanine	$-CH_3$	3.4
α-aminobutyric acid	$-CH_2CH_3$	2.7
leucine	$-CH_2CH(CH_3)_2$	3.2
glutamic acid	$-CH_2CH_2COOH$	2.3
phenylalanine	$-CH_2(C_6H_5)$	0.8
tyrosine	$-CH_2(C_6H_4OH)$	1.6
methionine	$-CH_2CH_2SCH_3$	2.3

a N-acetyl-DL-amino acids were used with the exception of N-acetyl-L-glutamic acid.

b After hydrolysis.

Table II. Product yields in the γ-radiolysis of N-acetyl-DL-alanine and poly-DL-alanine.

Product	G	
	N-acetylalanine	Polyalanine
ammonia (total)	3.4	3.6
amide	2.8	3.1
free	0.6	0.5
propionic acid	1.4	1.8
pyruvic acid	0.4	~1
acetaldehyde	0.8	~0.4
lactic acid	≤0.2	---
acrylic acid	trace	---
hydrogen	0.40	0.45

Table III. Ammonia and fatty acid yields in the γ-radiolysis of aliphatic N-acetylamino acid.

N-acetylderivative	G	
	(NH_3)	(RCH_2COOH)
glycine	2.6	1.2
alanine	3.3	1.5
α-aminobutyric	2.7	1.9

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LEGENDS FOR FIGURES

Fig. 1. Ammonia (O) and chloride-ion (●) yields as a function of chloracetate concentration in acetylalanine glass, $RCONHCH(R)COONa \cdot 2H_2O$.

Fig. 2. Reciprocal chloride-ion as a function of (acetylalanine)/(chloracetate) concentration ratio in the systems $RCONHCH(R)COONa \cdot 2H_2O$,(O); $RCONHCH(R)COONa \cdot 8H_2O$,(●).

Fig. 3. Effect of increasing water content on ammonia (O) and propionic acid (●) yields from acetylalanine in the system $RCONHCH(R)COONa \cdot nH_2O$. Values at n=o are for polycrystalline acetylalanine, RCONHCH(R)COOH.

Fig. 4. Ammonia (O) and chloride-ion (●) yields as a function of chloracetate concentration in 2M acetylalanine, pH7. The points (□) represent ammonia yields in the presence of 0.5M and 1.0M formate ion [e^-_{aq} + chloracetate, $k = 1.2 \times 10^9 M^{-1} sec^{-1}$, e^-_{aq} + acetylamine(pH7), $k = 1.1 \times 10^7 M^{-1} sec^{-1}$; OH + formate, $k = 10^9 M^{-1} sec^{-1}$; OH + acetylalanine (pH7), $k = 2.5 \times 10^8 M^{-1} sec^{-1}$ (ref 1,18,23)].

Fig. 5. Effect of naphthalene sulfonic acid on ammonia yields from 2M acetylalanine, pH7.

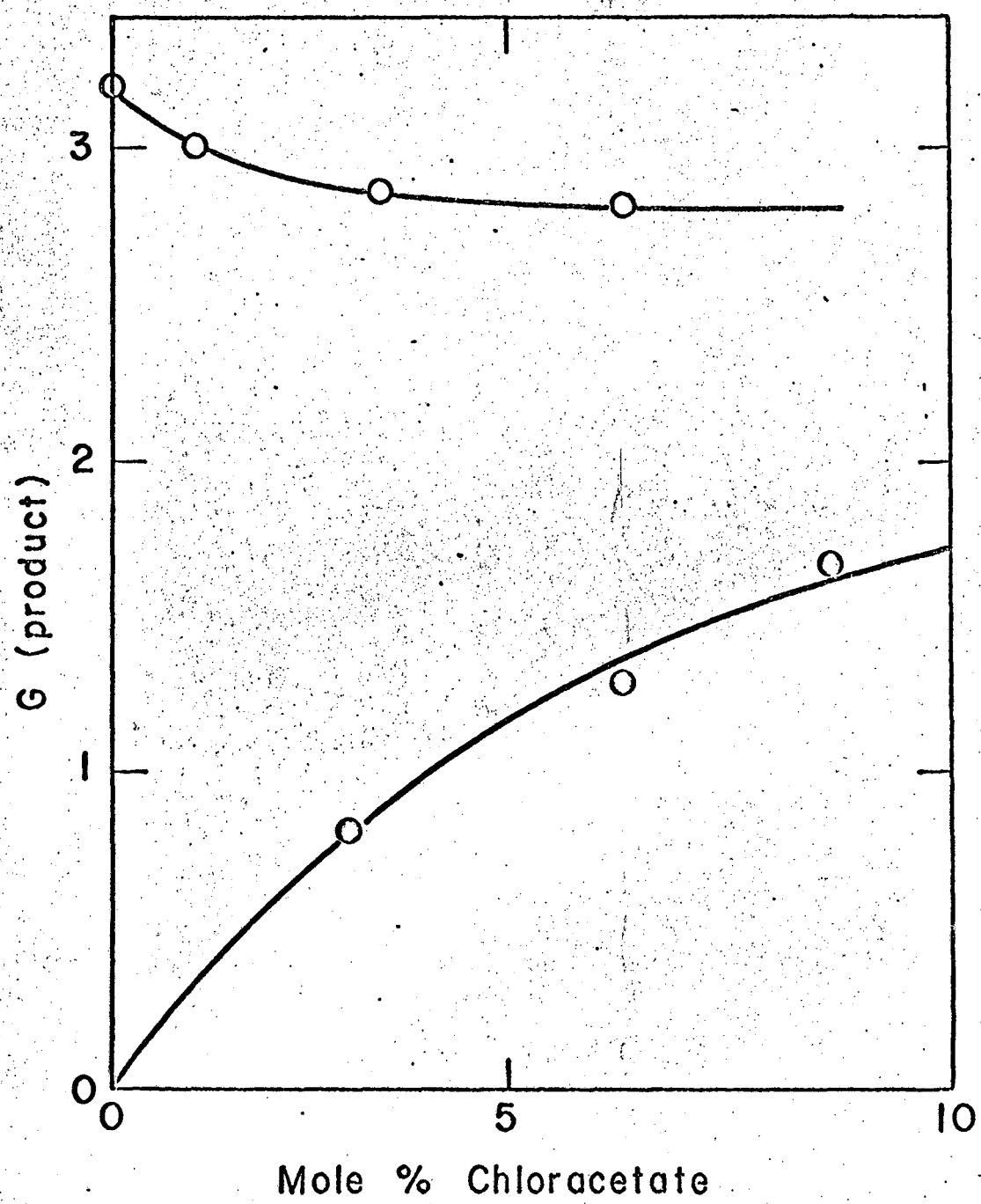

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Fig. 1

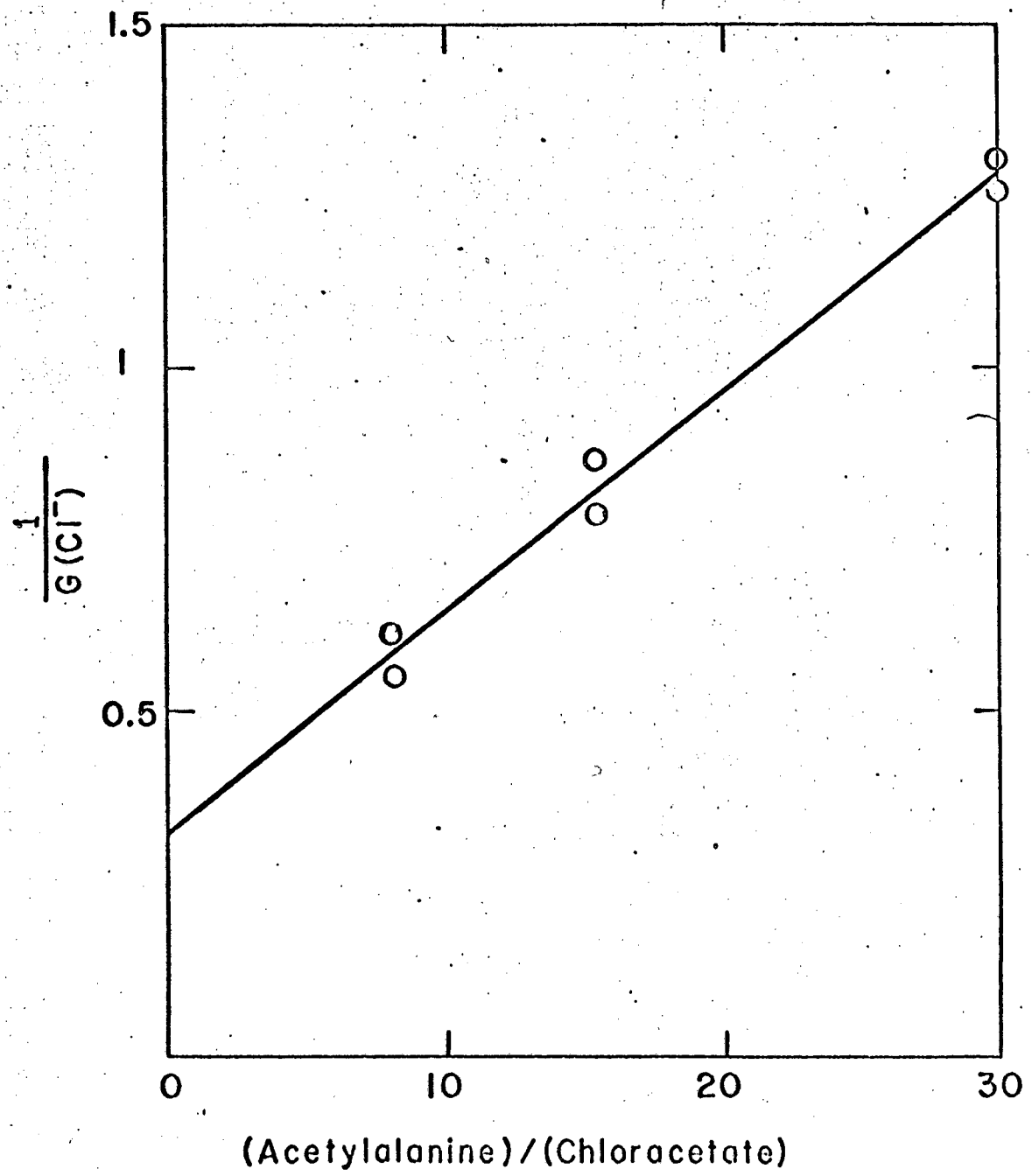

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Fig. 2

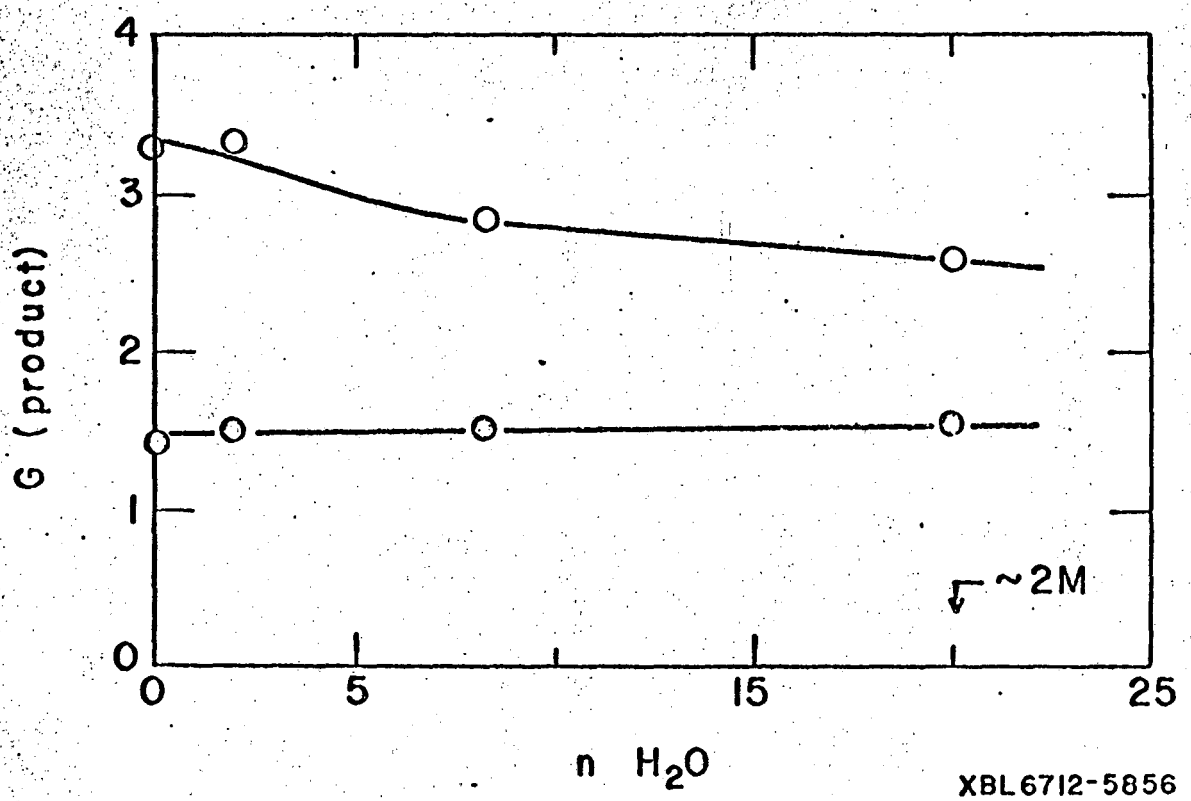

Fig. 3

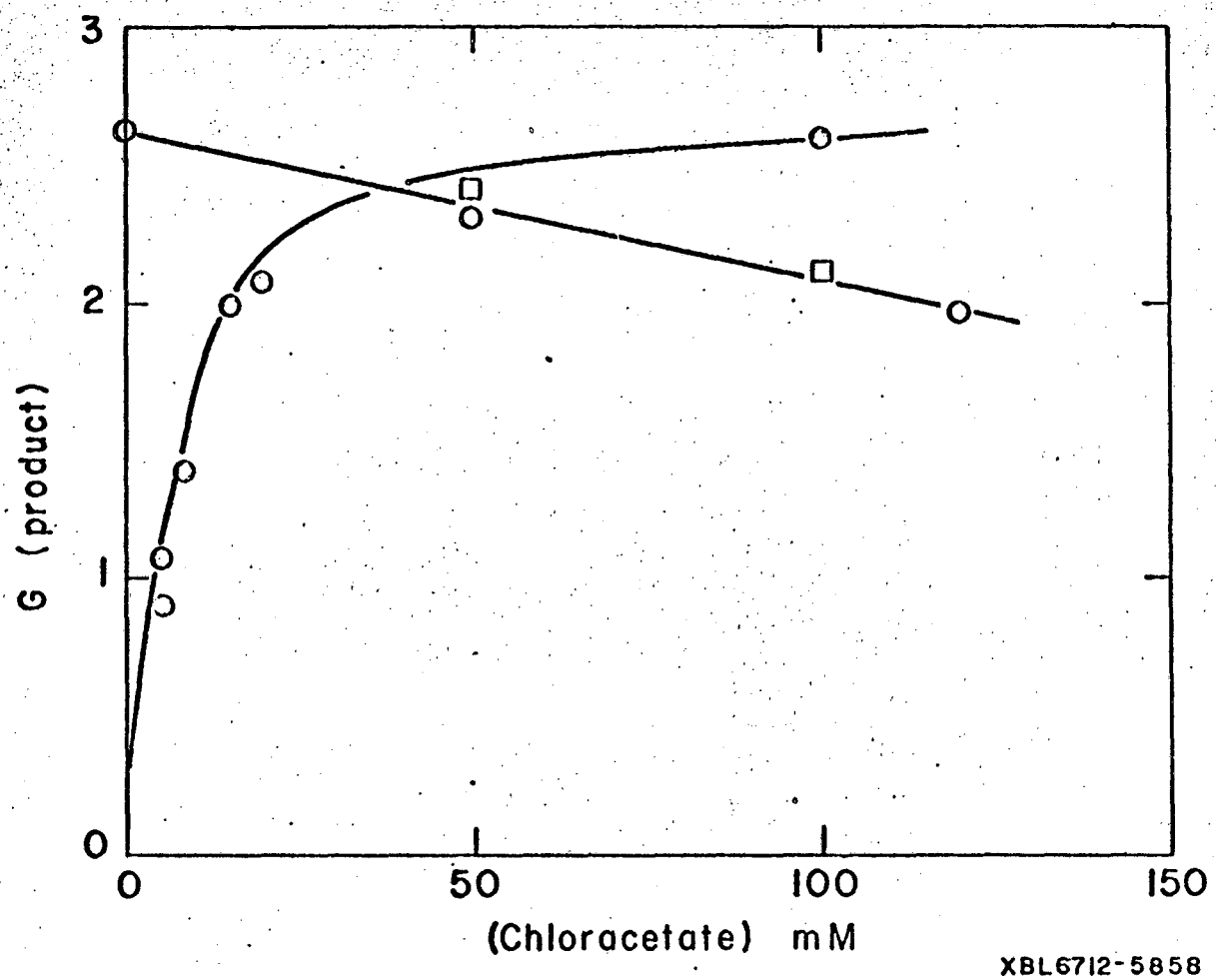

Fig. 4

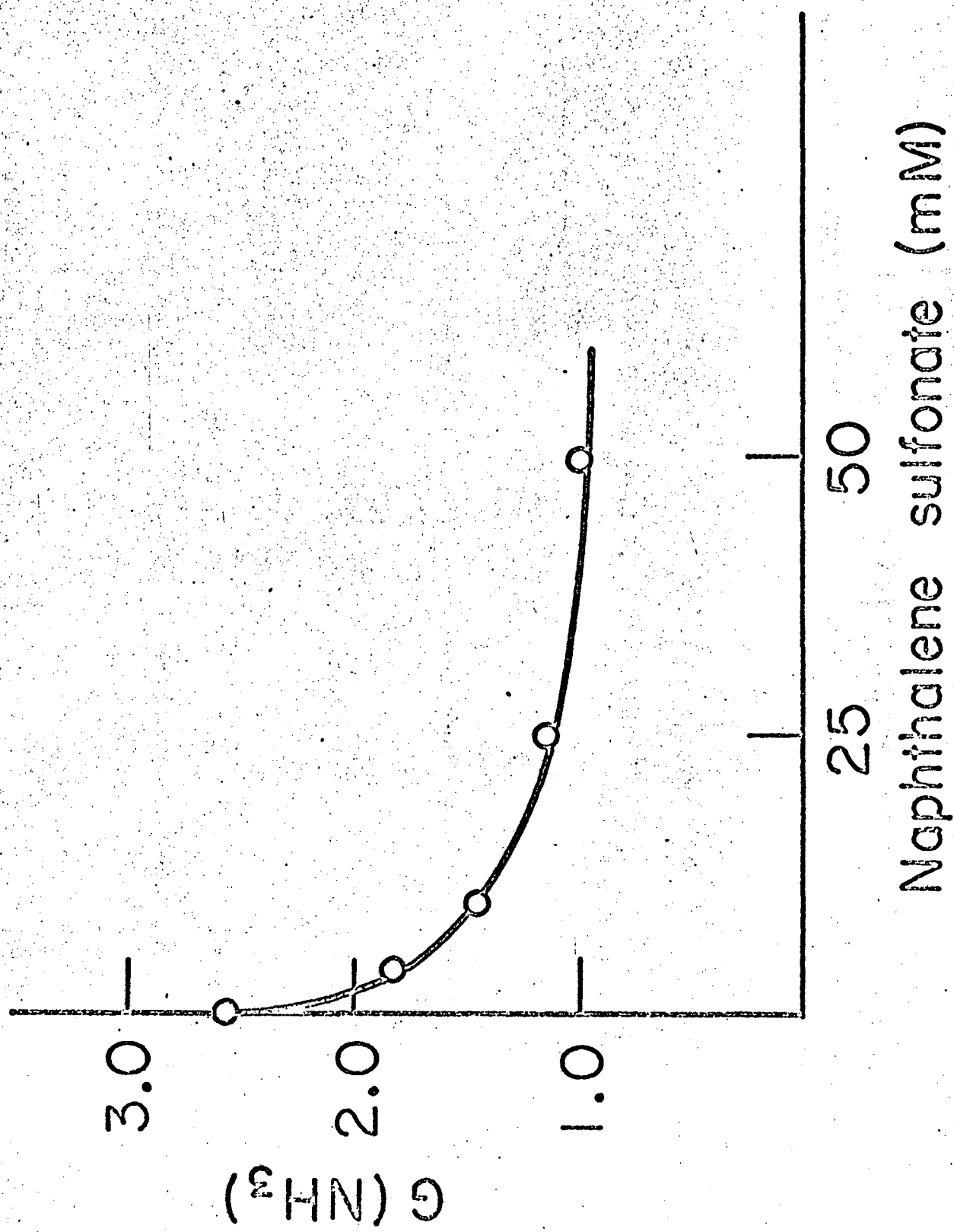

Fig. 5

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