Submitted to Journal of the American
Chemical Society

LBL-4989
Preprint c.1

HEAVY-ION RADIOLYSIS OF SOLID GLYCINE

T.-L. Tung, G. P. Welch, H. A. Sokol,
W. Bennett-Corniea, and W. M. Garrison

April 1976

Prepared for the U. S. Energy Research and
Development Administration under Contract W-7405-ENG-48

DISCLAIMER

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ABSTRACT

A study has been made of the effects of linear energy transfer (LET) in the heavy-ion radiolysis of solid glycine at dosages and dose-rates comparable to those employed in previous γ-ray studies. Beams of H^+, He^{+2}, Be^{+4}, C^{+6} and Ne^{+10} at energies of 10 Mev/nucleon were used. Yields of the major products, ammonia, acetic acid and glyoxylic acid were determined as a function of LET over the range .03 eV/Å to 60 eV/Å. A proposed reaction scheme is discussed in terms of current theories of track structure.

HEAVY-ION RADIOLYSIS OF SOLID GLYCINE[1]

T.-L. Tung, G. P. Welch, H. A. Sokol, W. Bennett-Corniea
and W. M. Garrison*

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

The increasing interest[2] in the effects of heavy-ion beams on biological systems emphasizes the need for detailed information on the effects of linear energy transfer (LET) in the radiation chemistry of biochemical compounds. Henriksen[3] has examined the effects of LET on the ESR spectra of free radicals formed in solid amino acids and peptides by heavy-ion beams, but no detailed radiation chemical studies of such systems have appeared to date.

We have chosen solid glycine for initial investigation because the mechanism of the γ-radiolysis of this biochemical compound has been formulated in detail[4, 5] i.e.

$$NH_3^+CH_2COO^- \rightsquigarrow (NH_3^+CH_2COO^-)^+ + e^- \qquad (1)$$

followed by

$$(NH_3^+CH_2COO^-)^+ \longrightarrow NH_3^+\dot{C}HCOO^- + H^+ \qquad (1a)$$

$$e^- + NH_3^+CH_2COO^- \longrightarrow NH_3 + \dot{C}H_2COO^- \qquad (2)$$

where $NH_3^+\dot{C}HCOO^-$ and $\dot{C}H_2COO^-$ represent the long-lived free radicals observed at room temperature by ESR spectroscopy.[6] On dissolution of the irradiated solid in O_2-free water, these radicals are removed essentially quantitatively through the reaction

$$NH_3^+\dot{C}HCOO^- + \dot{C}H_2COO^- \longrightarrow NH_2^+{=}CHCOO^- + CH_3COO^- \qquad (3)$$

The imino acetic, $NH_2^+=CHCOO^-$, is labile and hydrolyzes spontaneously

$$H_2O + NH_2^+=CHCOO^- \longrightarrow NH_4^+ + CHOCOO^- \qquad (4)$$

The over-all stoichiometry with γ-rays corresponds to $G(NH_3)\simeq 5$, $G(CH_3COOH)\simeq G(CHOCOOH)\simeq 2.5$.

We now have measure the yields of these reactions as a function of LET using beams of H^+, He^{+2}, Be^{+4}, C^{+6} and Ne^{+10}at energies of ~10 Mev/nucleon. Some physical parameters of these beams are summarized in Table I.

A modification of the standard beam optics of the LBL 88-inch cyclotron[7] was employed so that dosages and dose-rates are comparable to those employed in earlier γ-ray studies. Details of the irradiation procedures have been fully described in a recent publication.[8] The analytical techniques and procedures used in the present work were developed in our earlier studies.[5,9,10]

The effects of LET on product yields from solid glycine are summarized in Fig. 1. Over the LET range ~.03 eV/Å to ~10 eV/Å there is a steady decline in the yield of all products. However, at LET values above ~10 eV/Å the yields of acetic acid and glyoxylic acid become essentially independent of LET. Now it is well known[11-13] that fast charged particles lose energy to electrons of the absorbing media via (1) glancing collisions which have low energy loss ($\leq$ 100 eV) per event and via (2) knock-on collisions which give rise to energetic secondary electrons. The glancing collisions form spurs which contain several ion pairs in close proximity.[12, 14] With γ-rays the spurs are widely separated and in polar media most of the electrons escape the parent positive ions. In the present system they become trapped via reaction 2. When the LET of the radiation is increased, the spurs begin to overlap and charge recombination i.e.

$$(NH_3^+CH_2COO^-)^+ + e^- \longrightarrow (NH_3^+CH_2COO^-)^{\ddagger} \qquad (5)$$

can occur in competition with reaction 2. Hence, the product yields decrease as observed in Fig. 1. Above ~10 eV/Å the spurs coalesce to form a track core which is surrounded by a sheath or penumbra of lower ionization.[13, 15] The latter is formed by the energetic secondary electrons produced in knock-on collisions. It is in the penumbra that reaction 2 largely occurs. The finding that the yield of glyoxylic and acetic acids become independent of LET above ~10 eV/Å is consistent with the fact that the energy distribution of the secondary electrons ejected from the track core is the same for particles having the same velocity.[13] This is the case in the present study since all of the particles used have the same energy per nucleon. The fact that the limiting yield of glyoxylic and acetic acids at the higher LET values is essentially one-half the corresponding γ-ray values is in good accord with the theoretical conclusions that there is an equipartition of energy between knock-on collisions and glancing collisions.[12, 13]

The free radical yield continues to decrease with increasing LET over the entire range studied. We conclude that reaction 3 occurs in part within the solid at the higher LET values.

The ammonia yield, which on the basis of the reaction scheme given in equation 1-4 should be equal to the sum $G(CH_3COOH) + G(CHOCOOH)$ does show an inital decrease with increasing LET but does not fall to the anticipated values of $G \approx 2.5$. In fact, $G(NH_3)$ actually increases with

LET above ~10 eV/Å. It is clear that processes in addition to those given by equations 1-4 become increasingly important at the higher LET values. We presume that such processes occur in or near the track core and may involve reactions of excited species formed in the recombination reaction 5.[16] The nature of this "core" chemistry is presently under investigation.

Acknowledgment: We are indebted to the staff of the 88-inch cyclotron for assistance in the irradiations. We also thank Dr. A. Chatterjee for helpful discussions on the theory of track structures.

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1. This work was perfomed under the auspices of the U.S. Energy Research and Development Administration.

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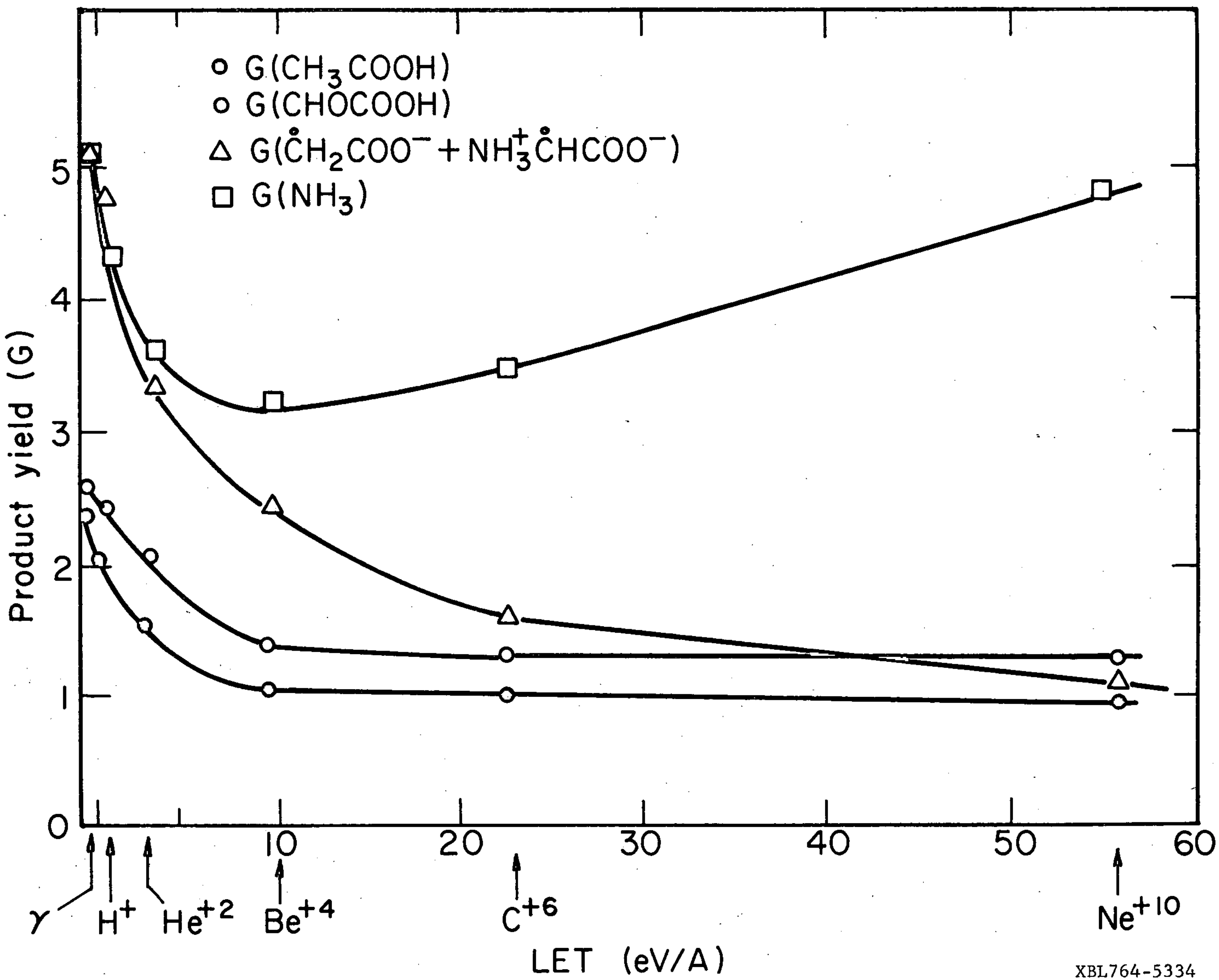
Table I: Range and LET of particles with energies of 10 MeV per nucleon

	H^{+}	He^{+2}	Be^{+4}	C^{+6}	Ne^{+10}
Particle energy (MeV)	10	40	90	120	200
Range (mg/cm^2)	110	110	75	45	35
LET (eV/Å)	0.7	2.8	10	23	56

Figure 1: Product yields as a function of LET in the radiolysis of solid glycine. Dose, 1.85×10^{20} eV/gm; dose rate, 6×10^{18} eV/gm-min. Radical yields are normalized to G = 5.2 as measured by Zimmer and Müller for the γ-radiolysis of solid glycine (ref. 17).



XBL764-5334

Fig. 1

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720