

Figure 1. Molecular structure of $(\text{Ph}_2\text{PCH}_3)_2\text{Au}_2\text{WS}_4$.

greatly different formal oxidation states, Au(I) and W(VI), in close proximity as they are in **6**.²²

Additional experiments have revealed that a like deoxygenation with tertiary phosphines cannot be applied to $\text{MoO}_2\text{S}_2^{2-}$ but the molybdenum analogues of **3** and **6** are readily obtained from $(\text{Ph}_3\text{PCH}_3)_2\text{MoS}_4$.

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- (10) diphos is 1,2-bis(diphenylphosphino)ethane.
- (11) **3**, Anal. Calcd (found): C, 50.36 (50.05); H, 4.20 (4.29); Cu, 10.25 (10.61); P, 10.00 (9.89); S, 10.33 (9.77); W, 14.85 (15.37); mol wt 1239 (744 in CHCl_3). Anal. for **4**: C, 46.98 (46.99); H, 3.92 (4.16); Ag, 16.27 (17.34); P, 9.33 (9.40); S, 9.64 (9.40); W, 13.86 (13.32). Anal. for **5**: C, 33.62 (33.64); H, 2.80 (3.11); Ag, 23.27 (23.50); P, 6.68 (6.65); S, 13.79 (13.45); W, 19.83 (20.13); mol wt, 928 (1019 in CHCl_3). Anal. for **6**: C, 28.21 (28.33); H, 2.35 (2.32); P, 5.61 (4.98); S, 11.57 (10.99); mol wt, 1106 (958 in CHCl_3). Analyses were performed by Schwarzkopf Laboratories.²³
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- (22) This, of course, begs the question of the actual oxidation states of the Au and W centers. We are currently studying this problem by x-ray photoelectron spectroscopy.
- (23) Certain commercial services have been identified in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the services identified are necessarily the best available for the purpose.

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Heavy-Ion Radiolysis of Solid Glycine¹

Sir:

The increasing interest² 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. Henriksen³ 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.

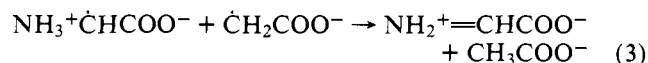
We have chosen solid glycine for initial investigation because the mechanism of the γ -radiolysis of this biochemical compound has been formulated in detail,^{4,5} i.e.



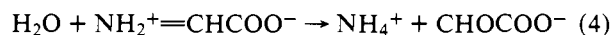
followed by



where $\text{NH}_3^+\dot{\text{C}}\text{HCOO}^-$ and $\dot{\text{C}}\text{H}_2\text{COO}^-$ 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



The imino acetic, $\text{NH}_2^+=\text{CHCOO}^-$, is labile and hydrolyzes spontaneously



The overall stoichiometry with γ -rays corresponds to $G(\text{NH}_3) \approx 5$, $G(\text{CH}_3\text{COOH}) \approx G(\text{CHOCOOH}) \approx 2.5$.

We now have measured 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 $\sim 10 \text{ MeV/nucleon}$. Some physical parameters of these beams are summarized in Table I.

A modification of the standard beam optics of the LBL 88-in. cyclotron⁷ 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}

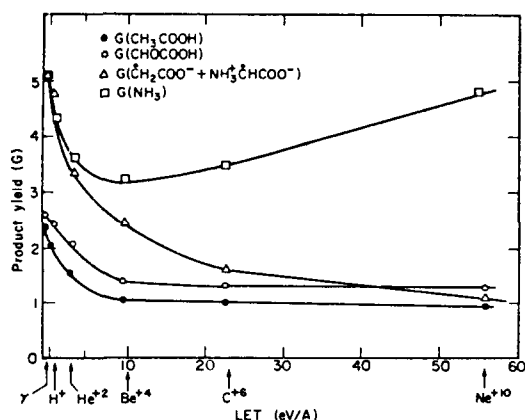
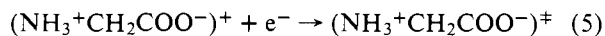


Figure 1. Product yields as a function of LET in the radiolysis of solid glycine: dose, 1.85×10^{20} eV/g; dose rate, 6×10^{18} eV/(g min). Radical yields are normalized to $G = 5.2$ as measured by Zimmer and Muller for the γ -radiolysis of solid glycine (ref 17).

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

The effects of LET on product yields from solid glycine are summarized in Figure 1. Over the LET range ~ 0.03 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 known¹¹⁻¹³ that fast charged particles lose energy to electrons of the absorbing media via (1) glancing collisions which have low energy loss (≤ 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.



can occur in competition with reaction 2. Hence, the product yields decrease as observed in Figure 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 eq 1-4 should be equal to the sum

$G(\text{CH}_3\text{COOH}) + G(\text{CHO}_2\text{COOH})$, does show an initial decrease with increasing LET but does not fall to the anticipated values of $G \approx 2.5$. In fact, $G(\text{NH}_3)$ actually increases with LET above ~ 10 eV/Å. It is clear that processes in addition to those given by eq 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.

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References and Notes

- (1) This work was performed under the auspices of the U.S. Energy Research and Development Administration.
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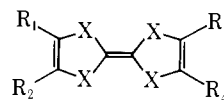
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Formation of Highly Conducting Organic Salts by Photooxidation of Heterofulvalene π -Donors in Halocarbon Solutions

Sir:

The charge transfer salts of heterofulvalene-type π -donors such as tetrathiafulvalene (TTF)¹ and its derivatives² with tetracyanoquinodimethane and halogen acceptors are currently a major focus of organic solid state research because of their unusually high electrical conductivities.³⁻⁵ In the course of crystal chemical studies of tetrathiafulvalinium-halide systems^{3b,6} we have observed an unusual photooxidation reaction of TTF and related π -donors in halocarbon solvents such as CCl_4 . The photooxidation reaction, which we report in this communication, provides a novel method for synthesizing⁷ high conductivity π -donor/halide salts, and moreover, gives important insight into some of the factors governing the photooxidative stability of π -donors in such solvents.



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