initial scans the current peaks due to the oxidation of I successively decrease in amplitude (due to exhaustion of I near the electrode), while those due to the redox couple of II increase (as the concentration of II builds up near the electrode). This demonstration of the oxidative coupling of I to form II is also observable in acetonitrile.

A surprising fact about the reversible redox couple for II is that it is a *two*-electron process. This was clearly demonstrated by cyclic coulometry. Closely related to this tetraaminobutadiene is tetrakis(dimethylamino)ethylene (III) which was studied extensively by Kuwata and Geske.[5] The cyclic voltammetry of III appears in Figure 3. Note that the two one-electron steps are separated by only 0.1 v for this compound.

We are presently studying the electrolytic oxidations of other aminoethylenes and of aromatic hydrocarbons and will report on these in the near future.

(5) K. Kuwata and D. H. Geske, *J. Am. Chem. Soc.*, **86**, 2101 (1964).

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Received December 5, 1967

The Radiation-Induced "Hydrolysis" of the Peptide Bond[1]

Sir:

We find that the γ radiolysis of oxygen-free solutions of simple peptides such as the N-acetylamino acids leads to liberation of the free amino acid as a major reaction product. As a specific example, the alanine[2] yield from N-acetylalanine in an evacuated solution at pH 7 increases abruptly with increasing solute concentration over the range 0.05–0.25 M and then levels off to a limiting value of G(alanine) $\simeq$ 1 at acetylalanine concentrations above 0.5 M as shown in Figure 1.

This radiation-induced liberation of free amino acid is quenched by second solutes such as hydronium ion, molecular oxygen, and chloroacetate ion, all of which are known to be effective scavengers of the hydrated electron, e_{aq}^-, formed in the radiation-induced step[3,4]

$$H_2O \longrightarrow H_2O_2, H_2, OH, H^+, e_{aq}^- \quad (1)$$

The effect of chloroacetate ion on G(alanine) from 1 M acetylalanine at pH 7 is shown in Figure 1, insert. The reciprocal-yield plot gives $k_2/k_3 = 1.9 \times 10^2$ for the ratio of the rate constants of the competing reactions

$$e_{aq}^- + RCl \longrightarrow R + Cl^- \quad (2)$$

$$e_{aq}^- + RCONHCHR_2 \longrightarrow (RCONHCHR_2)^- \longrightarrow \text{products} \quad (3)$$

This value is in good agreement with other measurements of the reactivity of e_{aq}^- toward these solutes.[5]

The evidence is then that the reducing species, e_{aq}^-, is specifically involved in the chemistry that leads to

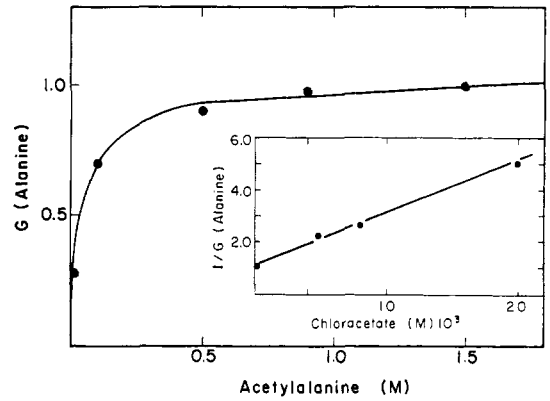

Figure 1. G(alanine) as a function of acetylalanine concentration in oxygen-free solution at pH 7 under γ rays. Insert: reciprocal yield plot of G(alanine) as a function of chloroacetate concentration in 1 M acetylalanine.

liberation of free alanine. Previous work has established that the oxidizing species, OH, is removed preferentially through H abstraction at the α-carbon position of acetylalanine

$$OH + RCONHCHR_2 \longrightarrow RCONH\dot{C}R_2 + H_2O \quad (4)$$

where $k_4 = 2.5 \times 10^8\ M^{-1}\ sec^{-1}$.[6] Addition of an OH scavenger such as formate ion ($k_{f+OH} = 2.5 \times 10^9\ M^{-1}\ sec^{-1}$)[4,7] at concentrations as high as 0.5 M has no effect on G(alanine) in 1 M acetylalanine.

Now, if the removal of e_{aq}^- *via* reaction 3 leads to reduction of the peptide linkage, *e.g.*

$$(RCONHCHR_2)^- + H_2O \longrightarrow R\dot{C}(OH)NHCHR_2 + OH^- \quad (5)$$

then it is clear that combination of $R\dot{C}(OH)NHCHR_2$ with like species or with the α-carbon radical $RCONH\dot{C}R_2$ would lead to formation of Schiff-base derivatives of the type $R(R')C(OH)NHCHR_2$ which compounds are labile with respect to the decomposition

$$R(R')C(OH)NHCHR_2 \longrightarrow R(R')CO + NH_2CHR_2 \quad (6)$$

The stoichiometry of reaction 6 would also be observed if the (Schiff base) radical $R\dot{C}(OH)NHCHR_2$ underwent the decomposition

$$R\dot{C}(OH)NHCHR_2 \longrightarrow R\dot{C}O + NH_2CHR_2 \quad (7)$$

before dimerization. In any event, the main point here is that the formation of alanine through net reduction of the peptide linkage in accord with the stoichiometry of reactions 6 and 7 requires the concomitant formation of ketonic products R(R')CO. Detailed chemical analyses[7] of the irradiated solutions reveal that the yield of such products is quite low with $G \leq 0.2$. Evidently reductive cleavage of the peptide bond does not yield the major part of the observed alanine even though the formation of this product is directly related to the attack of the reducing species, e_{aq}^-.

A concept that appears to provide a clue to the interpretation of the chemistry of the present system is that the radical products of e_{aq}^- and OH attack are subsequently removed not by dimerization (combination) but by disproportionation. Of course, disproportionation involving $R\dot{C}(OH)NHCHR_2$ and the α-carbon radical

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

(2) Alanine was identified chromatographically and assayed by the ninhydrin method; since ammonia is produced as a minor product and is "ninhydrin positive," a correction was made on the basis of a standard ammonia assay after the method of Conway.

(3) C. J. Hochanadel and R. Casey [*Radiation Res.*, **25**, 198 (1965)] report the following 100-ev yield for reaction 1: $G_{OH} = 2.59$, $G_{e_{aq}^-} = 2.58$, $G_H = 0.55$, $G_{H_2} = 0.45$, $G_{H_2O_2} = 0.72$.

(4) For a recent compilation of rate data, see M. Anbar and P. Neta, *J. Appl. Radiation Isotopes*, **17**, 493 (1967).

(5) R. L. S. Willix and W. M. Garrison, *Radiation Res.*, **32**, 452 (1967).

(6) M. A. J. Rodgers and W. M. Garrison, *J. Phys. Chem.*, in press.

(7) (a) B. M. Weeks, S. A. Cole, and W. M. Garrison, *ibid.*, **69**, 4131 (1965); (b) W. M. Garrison and B. M. Weeks, *Radiation Res. Suppl.*, **4**, 54 (1964); (c) H. L. Atkins, W. Bennett-Corniea, and W. M. Garrison, *J. Phys. Chem.*, **71**, 772 (1967).

would lead simply to a reconstitution of the parent peptide

$$R\dot{C}(OH)NHCHR_2 + RCONH\dot{C}R_2 \longrightarrow 2RCONHCHR_2 \quad (8)$$

However, since the reduced radical $R\dot{C}(OH)NHCHR_2$ is an amine species, it is likely to be in an adduct form in the presence of high concentrations of the peptide

$$R\dot{C}(OH)NHCHR_2 + RCONHCHR_2 \rightleftharpoons \begin{matrix} R\dot{C}(OH)NCHR_2 \\ | \\ RC(OH)NHCHR_2 \\ \dot{I} \end{matrix} \quad (9)$$

Removal of the adduct radical ($\dot{I}$) *via* the analog of reaction 8 leads to formation of a Schiff base (I) which as shown in eq 10 can rearrange to give alanine and diacetylalanine[8]

$$\begin{matrix} RCONCHR_2 \\ | \\ RC(OH)NHCHR_2 \\ I \end{matrix} \longrightarrow (R_2CO)_2NCHR_2 + NH_2CHR_2 \quad (10)$$

The diacetylamines are labile with respect to the hydrolysis

$$(R_2CO)_2NHCHR_2 + H_2O \longrightarrow RCOOH + RCONHCHR_2 \quad (11)$$

Our measurements of G(acetic) are in good agreement with this formulation. We find that the yield of free acetic acid is low, $G \leq 0.3$, and we also find that on mild differential hydrolysis of the irradiated solution additional acid is liberated to give G(acetic) $\simeq 1.5 \simeq$ G(alanine).

A detailed account of this work is in preparation and will appear in a forthcoming publication.

(8) Product I could, of course, be formed through combination of $R\dot{C}(OH)NHCHR_2$ with nitrogen radicals of the type $RCO\dot{N}CHR$. The latter are not produced through OH attack,[7b] but we cannot rule out the possibility that such species may be formed through "direct-action" processes at high solute concentrations.

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Received November 16, 1967

Photosensitized Isomerization of Azobenzene

Sir:

Hammond and Jones have reported[1] that sensitized *cis* → *trans* photoisomerization of azobenzene takes place when its solutions are irradiated in the presence of triphenylene, β-acetonaphthone, or 3-acetylpyrene. However, with all three sensitizers the photostationary states established contained only 1.5–1.8% *cis*, instead of not far from 50% as observed in the case of stilbene.[2,3] In the latter case the results were taken to indicate that both in direct and in sensitized photoisomerization considerable or even quantitative crossing into the triplet system occurs.[2,3]

We wish to report results which differ sharply from those quoted above and therefore lead to different conclusions. Unfortunately the absence of experimental details in Hammond's note makes it difficult to compare the procedures applied in the two investigations in order to explain the discrepancies.

In our experiments light at 313 nm was used at 25°. Preferential absorption of light at this wavelength was achieved by working at high sensitizer concentrations as compared with that of azobenzene. The concentration of the latter was 5×10^{-5} M throughout. The isomeric composition was determined from the absorbance at the shoulders around 330 and 345 nm. Sensitizers used were naphthalene and triphenylene. Toluene and methylcyclohexane were used as solvents and gave comparable results.

In a typical experiment, 2 ml of a solution of azobenzene in a regular 10-mm spectrophotometric cell was irradiated with light at 313 nm until the photostationary state was reached (80% *cis*). Solid triphenylene was then added to make the solution 0.02 M, and irradiation was continued until the new photostationary state was reached (25% *cis*). The solution was then heated to 90° to convert the azobenzene completely into the *trans* isomer, and irradiation was continued at 25°. The same photostationary state was attained. Under these conditions 8% of the total absorbed light is absorbed by the azobenzene and 92% by the triphenylene. Similar experiments with naphthalene gave the following results (naphthalene (M), % light absorbed by naphthalene, % *cis* isomer in photostationary state): 0.02, 60, 39; 0.1, 93, 26; and 0.5, 98.6, 22 ± 2. In order to further ensure the relative lack of importance of direct photoisomerization, and also to check on possible effects of fluorescent light emitted by the sensitizer, the solution of azobenzene only was irradiated at 313 nm through a 5-mm cell containing naphthalene or triphenylene, at the same concentration as used in the sensitization experiments, and placed in contact with the first cell. Under these conditions photoisomerization took place at a rate determined by the transmission of this "filter" solution at 313 nm, and the photostationary state attained was the same as that without the filter solution. With a 0.1 M naphthalene solution the rate of photoisomerization is reduced about 50-fold, and effects due to fluorescent light should be easily noticeable.

As pointed out,[1] the wide absorption range of azobenzene makes it impossible to carry out a "pure" sensitization experiment, *i.e.*, one in which light is absorbed only by the sensitizer. We believe that it is difficult to improve the experimental conditions in this respect much beyond those pertaining in a 0.5 M naphthalene solution.

The ratio *trans*:*cis* in the photostationary state seems to approach a value of 4 (corresponding to 20% *cis*). This ratio is equal[1] to the decay ratio of the two isomers and is in good agreement with the values 4 and 2 found by Zimmerman, *et al.*, for the direct photoisomerization of azobenzene.[4]

We conclude[5] that (1) a strong argument in favor of a crossing of the paths in the triplet-sensitized and in the direct photoisomerization of azobenzene can be made, based on the present results; (2) these results do not allow one to say *where* these paths cross, (3) one possibility is that azobenzene undergoes appreciable inter-

(1) L. B. Jones and G. S. Hammond, *J. Am. Chem. Soc.*, **87**, 4219 (1965).
(2) S. Malkin and E. Fischer, *J. Phys. Chem.*, **68**, 1153 (1964).
(3) G. S. Hammond, *et al.*, *J. Am. Chem. Soc.*, **86**, 3197 (1964).
(4) G. Zimmerman, L. Chow, and V. J. Paik, *ibid.*, **80**, 3528 (1958).
(5) We are grateful to one of the referees for expanding our original conclusions in a way with which we fully agree.