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EVIDENCE FOR CROSS-REACTION IN γ -RADIOLYTIC DECARBOXYLATION
OF CARBOXYLIC ACIDS IN CONDENSED STATES*

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Evidence for Cross-Reaction in γ -Radiolytic Decarboxylation of Carboxylic
Acids in Condensed States

David R. Howton and Guey-Shuang Wu

Abstract

In support of an earlier proposal that ejection of an electron from the carboxy group of a carboxylic acid might lead to decarboxylation of another molecule to which that ionized is H-bonded, Co^{60} γ -irradiation of the crystalline palmitic-stearic acid "compound" (in which the two substances are cross-paired) yields a pentadecane:heptadecane product mole-ratio greater than unity, in contrast to results obtained when the two acids are self-paired. The data obtained indicate that under the conditions employed, decarboxylation is 13% direct (intramolecular) and 87% crossed (intermolecular).

Evidence for Cross-Reaction in γ -Radiolytic Decarboxylation of Carboxylic Acids in Condensed States¹

(1) This paper is based on work performed under Contract AT(01-1)-GEN-12 between the Atomic Energy Commission and the University of California, Los Angeles, Calif.

Sir:

In discussing results of a study of the γ -radiolysis of oleic acid²

(2) D. R. Howton and G.-S. Wu, J. Amer. Chem. Soc., 89, 516 (1967).

we presented rationale for entertaining the possibility that decarboxylation of such substances in condensed states (involving essentially complete "dimerization" via inter-carboxy-group hydrogen bonding) might occur to an important extent by a process, the essential details of which may be represented as follows:

A particularly interesting feature of this mechanism (and one which suggested an approach to experimental substantiation) is the implication that ionization of one molecule (ACOOH) actually leads to decarboxylation of the other (BCOOH) to which it is H-bonded. We present here observations we feel are understandable only in terms of the involvement of some such intermolecular cross-reaction.

Since the extensiveness of decarboxylation experienced by long-chain saturated fatty acids per unit ionizing radiation absorbed is inversely re-

lated to chain length³, the relative amounts of the two saturated hydrocar-

(3) W. L. Whitehead, C. Goodman, and I. A. Breger, J. chim. phys., 48, 184 (1951); we have shown that the relationship (originally demonstrated by use of α -particle irradiation) holds also for γ -irradiation.

bons (e.g., AH and BH) produced by irradiation of mixtures of homologous fatty acids (e.g., ACOOH and BCOOH) would be expected to be influenced by whether the two components are self- or cross-paired in the condensed state involved, and by whether the mode of decarboxylation is either direct or crossed in the sense indicated above. Thus the mole-ratio of pentadecane to heptadecane obtained by irradiation of an equimolar mixture of palmitic and stearic acids would be expected to be independent of the nature of the pairing in the condensed state if the hydrocarbons arose solely by direct mechanism(s), but to be inverted if cross-pairing and cross-reaction were involved.⁴

(4) The objective outlined here would, of course, have been thwarted if the G-yields of hydrocarbons from the homologs happened to be too nearly exactly inversely related to their mixture-electron fractions; they were not.

Taking advantage of the happy and well-documented⁵ fact that cooling

(5) See G. Degerman and E. von Sydow, Acta Chem. Scand., 12, 1176 (1958).

equilibrated equimolar melts of palmitic (P) and stearic (S) acids yields a crystalline "compound" of the substances comprised entirely of cross-paired H-bonded "dimers" (P-S), we exposed one sample of such material and another differing only in that the finely-divided crystalline substances were simply thoroughly admixed (and thus consisted solely of self-pairs: P-P and S-S), thermostatted at 10° to prevent melting, to 1 Mrad of Co⁶⁰

γ -radiation. The relative quantities of penta- (C_{15}) and heptadecane (C_{17}) present in each of the two irradiated materials was then determined by conventional gas chromatography. (In order to minimize possible alteration of composition arising from differences in volatility of the two hydrocarbons, the irradiated solids were dissolved in minimal quantities of chloroform-methanol and samples of the resulting solutions injected directly into the chromatographic apparatus.) The following data were obtained:

<u>nature of mixture</u>	<u>moles C_{15}/moles C_{17}</u>
self-paired	0.955 ± 0.0037^6
cross-paired	1.035 ± 0.0037^6

(6) Standard deviation of 5 runs in each case, reflecting reproducibility of gas chromatographic analyses.

Clearly, the manner in which palmitic and stearic acid molecules are paired in the solid state influences the probability of their decarboxylation, and in a way that is consistent with the proposed cross-reaction mechanism. (Some "direct" decarboxylation - initiated, for example, by homolysis of C-C, C-O, or O-H bonds of the carboxy group - presumably takes place concomitantly. If the proportion of decarboxylation occurring via crossed vs. direct mechanisms is assumed to be the same for both acids, it is easily calculated on the basis of these data that about 87% cross-decarboxylation is involved.)⁷

(7) At the low dose of irradiation employed here (less than 0.1% of the original carboxylic acid is converted to hydrocarbon), such interpretations are not complicated by secondary-reaction destruction of the hydrocarbons or by significant distortion of the original equimolarity of the acids.

It should be pointed out that the unequal molar amounts of C_{15} and

C₁₇ hydrocarbons obtained from the cross-paired mixture excludes as a significantly important eventuality the transfer of an electron from the normal carbonyl oxygen of the H-bonded carboxy group pair to that which is electron-deficient, i.e.,

Such a rearrangement, if extensive prior to the hydrogen atom transfer which precipitates decarboxylation, would be expected to give equimolar amounts of hydrocarbons from cross-paired acids as closely similar in structure as palmitic and stearic. Although no covalent-bond pathway for such an electron exchange is available, this might take place by tunneling. We estimate⁸ that such an electron relocation should occur at

(8) The authors are indebted to Dr. Hardin Strickland of This Laboratory for assistance in carrying out this calculation.

a frequency near that characteristic of stretching of the O-H bond involved (about 10^{14} sec⁻¹); since the experimental evidence indicates that the radical cation intermediate is not in fact appreciably symmetrized, we conclude that the hydrogen atom transfer is virtually immediate.

In 1969, Schwartz et al.⁹ pictured decarboxylation induced by ioniz-

(9) R. N. Schwartz, M. W. Hanna, and B. L. Bales, J. Chem. Phys., 51, 4336 (1969).

ing irradiation of crystalline acids as involving a cationic radical intermediate having the electron hole localized on the hydroxylic (rather than the carbonyl²) oxygen of the carboxy group, converted to a carboxy radical by transfer of a proton from the ionized molecule to its H-bond neighbor. This sequence of events has been accepted by a number of in-

investigators apparently unaware of our earlier proposal.^{2,10} The ques-

(10) See, for example, M. Iwasaki, K. Minakata, and K. Toriyama, J. Amer. Chem. Soc., 93, 3533 (1971), and other references cited therein.

tion of which oxygen atom of the carboxy group bears the electron deficiency is crucial with respect to whether the ensuing decarboxylation is direct (in the sense that the ionized carboxy group is that which is lost) or crossed. Evidence presented here supports our original conclusion (on other grounds) that the electron hole is actually localized at the carbonyl oxygen of the ionized carboxy group.

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