

P, 10.00. Found: P, 9.78). Di-*n*-octylphosphine oxide, m.p. 85–6° (lit.⁶ m.p. 85°) was characterized by its reaction with acrylonitrile to give 2-cyanoethyl-di-*n*-octylphosphine oxide, m.p. 51–52° (lit.⁷ m.p. 53.4–54.2°). Bis-(2-cyanoethyl)-phosphine oxide, m.p. 98–99°, (calcd. for C₈H₉N₂OP: C, 46.15; H, 5.80; P, 19.84. Found: C, 46.32; H, 5.95; P, 19.94) was characterized by reaction with chloral hydrate to give bis-(2-cyanoethyl)-1-hydroxy-2,2,2-trichloroethylphosphine oxide, m.p. 159–160° dec. (calcd. for C₈H₁₀Cl₃N₂O₂P: C, 31.65; H, 3.32. Found: C, 31.76; H, 3.35). Additional examples and experimental details will be given in a subsequent publication.

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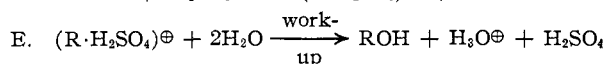
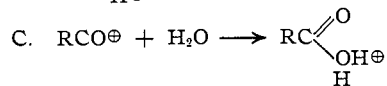
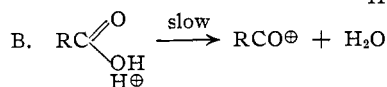
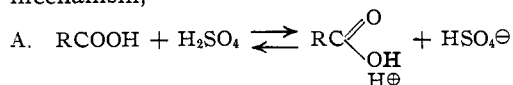
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ISOTOPIC EVIDENCE FOR THE MECHANISMS OF DECARBONYLATION OF THREE CARBOXYLIC ACIDS IN SULFURIC ACID

Sir:

As reaction mechanisms are often determined from the form of the observed acid catalysis, it is significant that the mechanism¹ of decarbonylation of triphenylacetic acid proposed on this basis is not supported by isotopic evidence. Complete equilibrium of the oxocarboxonium ion with water¹ and carbon-carbon bond cleavage as the rate determining step¹ are not supported since: (I) this decarbonylation in oxygen-18 enriched 95.5% sulfuric acid yielded carbon monoxide having an oxygen-18 enrichment of only about one-fifth that of the sulfuric acid,² and (II) no measurable isotope effect was found in the decarbonylation of triphenylacetic-2-C¹⁴ acid.

For the decarbonylation of formic acid the mechanism,³



accounts for the facts: (III) log of pseudo-first order rate constant linearly related to H_0^3 ; (IV) Large carbon-14 isotope effect ($k_{12}/k_{14} = \text{ca. } 1.09$),⁴

(1) N. C. Deno and R. W. Taft, *THIS JOURNAL*, **76**, 248 (1954).

(2) Although the two oxygen positions in carboxylic acids are not exactly equivalent, they should rapidly equilibrate through the symmetrical form, $\text{R}-\text{C} \begin{array}{l} \text{OH} \\ \parallel \\ \text{OH} \end{array}$. Hence, the proposed¹ equilibrium involving the oxocarboxonium ion and water should result in completely enriched carbon monoxide.

(3) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 283.

(4) G. A. Ropp, A. J. Weinberger and O. K. Neville, *THIS JOURNAL*, **73**, 5573 (1951); H. Eyring and F. W. Cagle, Jr., *J. Phys. Chem.*, **56**, 889 (1952).

(V) secondary deuterium isotope effect ($k_H/k_D = \text{ca. } 1.5$) with formic-*d* acid, undoubtedly due to stretching of the carbon-hydrogen bond during the slow step, B, and (VI) carbon monoxide of normal isotopic composition formed during reaction in oxygen-18 enriched sulfuric acid. Step C fails to occur because of its unfavorable competition with D, the rapid proton transfer to the sulfuric acid.

For the triphenylacetic acid decarbonylation the scheme, A, B, C, D, E, adequately accounts for facts I and II. Some back reaction of the oxocarboxonium ion with water, C, can occur by favorably competing with D which is an attack by sulfuric acid on the hindered number 2 carbon atom with ejection of carbon monoxide, and which is understandably slower than the analogous proton transfer in the formic acid decarbonylation. Since the oxygen-18 study indicates that C is slower than D, however, the mechanism is closer to that of formic acid³ than to the other extreme proposed by Deno and Taft.¹ The reported^{5,6} non-integral slope of the plot of $\log k$ vs. H_0 may be due to the intermediate character of the mechanism with neither B nor D strictly rate controlling.

The proposed mechanism⁶ of decarbonylation of benzoylformic acid can explain the results of isotopic studies: (VII) the large isotope effect⁷ with benzoylformic-1-C¹⁴ acid ($k_{12}/k_{14} = \text{ca. } 1.1$) due to carbon-14-oxygen bond cleavage in the rate step, VIII. A smaller effect ($k_{12}/k_{14} = \text{ca. } 1.036$) with benzoylformic-2-C¹⁴ acid, probably due to the effect of isotopic substitution at the number 2 carbon on the equilibrium constant of the reversible protonation involving the *alpha*-keto group, and IX. unenriched carbon monoxide from decarbonylation of benzoylformic acid in oxygen-18 enriched sulfuric acid, reasonable by analogy with the formic acid decarbonylation mechanism.

Non-radioactive carbon monoxide from decarbonylation of benzoylformic-2-C¹⁴ acid confirmed an earlier report⁸ that the carbon monoxide came only from the carboxyl group.

Helpful suggestions of John D. Roberts and F. A. Long are acknowledged.

(5) L. P. Hammett, *Chem. Revs.*, **16**, 67 (1935).

(6) W. W. Elliott and D. L. Hammick, *J. Chem. Soc.*, 3402 (1951).

(7) B. Fingerman and M. Lemmon, *Bio-Organic Chemistry Report*, Radiation Lab., Univ. of California, Berkeley, Calif., 1958, UCRL-8204.

(8) K. Banholzer and H. Schmid, *Helv. Chim. Acta*, **39**, 548 (1956).

(9) Chemistry Division, Oak Ridge National Laboratory, Operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

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INTRAMOLECULAR HYDROGEN BONDING INVOLVING DOUBLE BONDS, TRIPLE BONDS AND CYCLOPROPANE RINGS AS PROTON ACCEPTORS

Sir:

We wish to report evidence which demonstrates the occurrence of intramolecular hydrogen bonding between proton donors and unsaturated linkages, including cyclopropane rings, as proton acceptors. Recently, similar observations have been reported for intramolecular interactions between hydroxyl