

completely utilized, II could not be found. This evidence suggests that the reaction to form IV proceeds through II.

In previous papers from these laboratories,^{1,2,3,10} 6 and 11 hydroxylation and reduction of the double bond in the A ring by microorganisms have been described. The present communication describes the formation of 4-androstene-3,17-dione from C₂₁ steroids. It is interesting to note that these metabolic end products from steroidal substrates are similar to those produced by higher vertebrates.^{11,12,13}

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HYDROLYTIC POLYMERIZATION OF ZIRCONIUM(IV)¹

Sir:

Granér and Sillén² suggested that in the hydrolysis of Bi(III) a continuous series of particles is formed, all in equilibrium with each other and ranging in size from monomers to "infinitely" large polymers, the exact distribution depending on acidity and concentration. Recently Connick and Reas³, in an attempt to interpret solvent extraction data on Zr(IV), advanced the same hypothesis of continuous polymerization and equilibrium between the species and postulated the existence of high molecular weight particles in acidic solutions of Zr(IV). Other workers^{4,5,6} drew the conclusion that only low molecular weight polymers are formed in strongly acidic media. High molecular weight polymers, not in equilibrium with the more "normal" species, are apparently formed under considerably drastic conditions (*e.g.*, lower acidity or after boiling).⁷

Since the assumption that high molecular weight polymers are in equilibrium with low molecular weight polymers and monomers appears rather im-

(1) This document is based on work performed for the Atomic Energy Commission at the Oak Ridge National Laboratory: "Hydrolytic Behavior of Metal Ions. II." previous paper, *THIS JOURNAL*, **72**, 3901 (1950).

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(6) B. A. Lister and L. A. McDonald, *J. Chem. Soc.*, 4315 (1952).

(7) See, *e.g.*, R. Ruer, *Z. anorg. u. allgem. Chem.*, **43**, 282 (1905).

probable and since measurement of the acidity of ZrCl₄ solutions⁸ made it unlikely that an infinite series of polymers exists at high acidities, equilibrium ultracentrifugations of Zr(IV) were carried out in chloride and perchlorate solutions.⁹ The data were recently augmented and reanalyzed by a modification of the method of Lamm¹⁰ which was suggested to us by Professor George Scatchard, details of which will be published separately. In this computation the charge of the polymer units was considered, and estimates of this charge were obtained by ultracentrifugations under a variety of conditions. Centrifugation of 0.05 *M* Zr(IV) solutions in 1 *M* HCl–1 *M* MCl (where *M* was Li, Na and Cs) revealed the existence of only one principal species of Zr(IV) with an apparent degree of polymerization of 3.0 and charge $Z' < 1$ per monomer unit. At considerably higher and lower acidities (3 *M* HCl and 0.1 *M* HCl–1.9 *M* NaCl) mixtures were found with apparent degree of polymerization varying between *ca.* 2 to 2.6 (3 *M* HCl) and 4 to 5.4 (0.1 *M* HCl).

Similar low degrees of polymerization were found in ultracentrifugations in perchlorate solutions (1 *M* HClO₄–1 *M* NaClO₄). In this medium the zirconium particles appeared to carry a considerable charge and hence preliminary estimation of the degree of polymerization is somewhat more uncertain than for the chloride solutions. The most probable degree of polymerization for 0.05 and 0.12 *M* Zr(IV) solutions in this medium was 3, with an outside possibility that it may be as high as 4.5. There was no indication of an increase in degree of polymerization with concentration. These results may be compared with the (weight average) degrees of polymerization (N_w) estimated by Connick and Reas.³ These authors report $N_w = 18$ for a considerably more dilute solution (0.03 *M* Zr(IV)–1 *M* HClO₄–1 *M* LiClO₄) and a value of N_w between 10 and 300 at a higher acidity (0.17 Zr(IV)–2*M* HClO₄).

The results of the ultracentrifugation experiments described here thus indicate that Zr(IV) in strongly acidic solutions ($M H^+ > 0.1$) does not show continuous polymerization with high molecular weight products but rather forms only low molecular weight polymers with trimers apparently predominating at acidities near 1 *M*.

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(9) J. S. Johnson and K. A. Kraus, Reports ORNL-607 (1949), ORNL-1053 (1951).

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DPNH-CYTOCHROME REDUCTASE, A FERRO-FLAVO- PROTEIN¹

Sir:

Within the past year several flavoprotein enzymes have been shown to contain heavy metals as part of their prosthetic groups. Copper was identified as a constituent of butyryl CoA dehydrogen-

(1) Paper IV in a series entitled Studies on Diphosphopyridine Nucleotide-Cytochrome c Reductase. For paper III see L. P. Vernon, H. R. Mahler and N. K. Sarkar, *J. Biol. Chem.*, **199**, 598 (1952).