N, 20.27. Found: C, 17.42; H, 5.98; B, 38.87; N, 19.91). The latter was quite impact sensitive. The exact empirical formulas, with respect to hydrogen, are not known. A Raney nickel-catalyzed hydrogenation of the above two oxazahydroborate salts removed oxygen from the materials. The infrared spectra of the new products suggest that no N-H linkages are present, in contrast to the reduction product of  $B_{14}H_{12}NO^{-2}$ . Further characterization of these materials is in process.

Anal.  $[B_{10}H_{\vartheta}N_2 \cdot N(CH_3)_4]$ : calcd.: C, 21.89; H, 9.65; B, 49.30; N, 19.15. Found: C, 21.62; H, 9.54; B, 50.01; N, 19.24.  $[B_{20}H_8N_3 \cdot N(CH_3)_4]$ : calcd.: C, 20.67; H, 8.67; B, 46.55; N, 24.10. Found: C, 19.96; H, 8.42; B, 47.02; N, 23.91.

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ROHM & HAAS COMPANY REDSTONE ARSENAL RES. DIV. HUNTSVILLE, ALABAMA RECEIVED JULY 14, 1961

## MOLECULAR DETACHMENT OF HYDROGEN CHLORIDE IN THE PHOTOLYSIS OF CIS-1,2-DICHLOROETHYLENE<sup>1</sup>

Sir:

Recently<sup>2,3</sup> data have been published on molecular detachment processes in the vacuum ultraviolet photolysis of gaseous hydrocarbons. We have now obtained evidence that the molecular detachment of hydrogen chloride may be important in photochemical decompositions of chlorine containing compounds. Photolysis of *cis*-1,2-dichloroethylene indicates that these primary processes occur

$$cis-C_2H_2Cl_2 + h\nu \longrightarrow C_2H_2 + 2Cl \qquad (1a)$$

$$\longrightarrow$$
 C<sub>2</sub>HCl + HCl (1b)

The evidence for steps 1a and 1b is based upon the following facts. The rates of formation of  $C_2H_2$  and  $C_2HC1$  are directly proportional to the incident light intensity. This indicates that these products are not formed by free radical disproportionation reactions. The rates of formation of  $C_2H_2$  and  $C_2HC1$  are not reduced by the addition of isobutylene and of iodine as free radical scavengers. On the other hand, free radical reactions, such as the formation of *trans*-1,2-dichloroethylene, are severely reduced by the addition of free radical scavengers. *trans*-1,2-Dichloroethylene is produced to a large extent by the reactions.

$$cis-C_{2}H_{2}Cl_{2} + Cl \longrightarrow C_{2}H_{2}Cl_{2} *$$

$$C_{2}H_{2}Cl_{3} * \longrightarrow cis-C_{2}H_{2}Cl_{2} + Cl$$

$$\longrightarrow trans-C_{2}H_{2}Cl_{2} + Cl$$

Photochemical experiments using the full light of the Hanovia medium pressure arc (Type 16 A 13) yield a value of about 9 for the ratio  $C_2H_2/C_2HCl$ .

(1) This investigation was supported, in part, by the U. S. Atomic Energy Commission.

(2) H. Okabe and J. R. McNesby, J. Chem. Phys., 34, 668 (1961).

This ratio is reduced to about 3.3 if the light is transmitted through Corning filter No. 9-54 (transmitting above 2200 Å.). This indicates that C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>HCl originate from different electronic excitation levels. Since primary step 1a undoubtedly is more endothermic than step 1b it would be expected that lower wave lengths favor step 1a over step 1b as observed. In determining the ratio  $C_2H_2/C_2HC1$  by gas chromatography we have assumed that  $C_2HCI$  and  $C_2H_3Cl$ have the same sensitivity. This is an approximation and most likely the actual values for  $C_2$ - $H_2/C_2HC1$  will be somewhat lower than reported here. Further confirmation for steps 1a and 1b was obtained from mass spectrometer data which indicate that in the presence of free radical scavengers HCl but not Cl<sub>2</sub> is produced. This is in agreement with observations by Mahncke and Noyes.<sup>4</sup> These authors observed the production of HCl in the photolysis of cis-C<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub> but did not obtain positive evidence for the production of  $Cl_2$ .

It is possible that primary step 1a may occur in two steps as suggested by Futrell and Newton<sup>5</sup> in the liquid phase radiolysis of symmetrical dichloroethylenes

$$C_2H_2Cl_2 + h\nu \longrightarrow C_2H_2Cl^* + Cl \qquad (1c)$$

$$C_2H_2Cl^* \longrightarrow C_2H_2 + Cl$$
 (1d)

At the present time it is not possible to discriminate between this process and the simultaneous ejection of two chlorine atoms when the acetylene bond is formed as indicated by step 1a.

Our data show a great similarity between radiation chemistry data and conventional photochemical data. The radiolysis of symmetrical dichloroethylenes in the liquid phase has been studied by Futrell and Newton.<sup>6</sup> They observed  $C_2H_2$ ,  $C_2HCl$  and HCl as the major volatile products and explain their formation by steps 1b, 1c and 1d. Similar results have been obtained for the  $\gamma$ -ray radiolysis of gaseous cis- $C_2H_2Cl_2$  where  $G_{C_3H_2}$  and  $G_{C_3HCl}$  were found to be independent of the presence or absence of free radical scavengers.<sup>6</sup>

It is also clear that steps 1a and 1b are similar to steps 2a and 2b

$$C_2H_4^* \longrightarrow C_2H_2 + H_2 \qquad (2a)$$

$$C_2H_4^{**} \longrightarrow C_2H_2 + 2H \qquad (2b)$$

which have been shown to occur in the vacuum ultraviolet photolysis of ethylene<sup>3</sup> and which steps most likely play a major role in the radiolysis of ethylene.

At this time we have no information *pro* or *con* regarding possible primary step 1e, suggested by Mahncke and Noyes.<sup>4</sup>

$$cis-C_2H_2Cl_2 + h \rightarrow C_2H_2Cl + Cl$$

We expect that further investigations will yield information regarding step 1e. We are

(4) H. E. Mahneke and W. A. Noyes, Jr., J. Am. Chem. Soc., 58, 932 (1936).

<sup>(3)</sup> L. M. Dorfman and M. C. Sauer, Jr., presented at the 189th National Meeting of the American Chemical Society at St. Louis, Mo., 1961.

<sup>(5)</sup> J. H. Futrell and A. S. Newton, *ibid.*, 82, 2676 (1960).
(6) M. H. J. Wijnen, to be published.

also investigating the photolysis of  $trans-C_2H_2-Cl_2$  and of  $CH_2$ — $CCl_2$  in order to obtain information on how steps 1a and 1b depend on the position of the chlorine atoms in dichloroethylene.

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## BOOK REVIEWS

Mineral Metabolism. An Advanced Treatise. Volume I. Principles, Processes, and Systems. Part A. Edited by C. L. COMAR, Cornell University, Ithaca, New York, and FELIX BRONNER, Hospital for Special Surgery, Cornell Medical Center, New York, New York. Academic Press Inc., 111 Fifth Avenue, New York, 3, N. Y. 1960. xv + 416 pp.  $16.5 \times 23.5$  cm. Price, \$12.00.

Not in 20 years has a broad summary of mineral metabolism been attempted; it is time that the rich rewards of isotope studies and the applications of the modern concepts of bodily mechanics be put down for the "research scientists and advanced students in biology, medicine and agriculture." Comar and Bronner have enlisted the aid of acknowledged leaders in their respective fields to do the putting. The breadth of this now formidable task is encompassed in two volumes; this is part A of the first volume: "Principles, Processes, and Systems." Part B will add discussions of hormonal controls, minerals in non-osseous systems, bones and teeth, and interrelations with enzymes. Volume II will present summaries by elements: phosphorus, calcium, strontium, et al.

For Volume I, part A, Franklin C. McLean introduces *the theme:* the complex interplay of factors in the dynamic "internal environment" described as homeostasis, and *the task:* to search for the principles entering into or governing the steady states, to describe the processes in simplest terms, and to learn by what systems the processes are carried out.

A reader interested in more than a single question or a phase would do well to begin with chapter 7, "Body Fluid Dynamics," which describes the fundamental principles of exchange between body fluids. The extended definitions of "Thermodynamic Principles and Concepts," chapter 2, supply the pertinent mathematical generalizations that have been applied to metabolic kinetics. Chapter 3, "Cybernetic Aspects," develops "the principles of feedback theory, servo theory and information theory," and while no major accomplishments are claimed to date, these ideas are helpful in thinking about metabolic processes. Because a chelated metal ion exhibits properties differing markedly from those of the uncomplexed ion, the properties of chelates and the factors influencing chelation are given in some detail (chapter 4). Biological implications are not discussed. Chapter 5, "Compartmental Analysis," supplies a needed summary of the extended (and unassembled) kinetics that have proved in a few instances to give strong conceptual support for a plausible interpretation of events. Derivations are reasonably complete and the text is explicit. The last of the chapters on generalities (chapter 6) discusses "Ion Transport" and the electrical and energetic corollaries.

The final three chapters deal in a quantitative and lucid manner with the multitudinous events in "Intestinal Absorption and Excretion," "Renal Excretory Mechanisms" and "Extrarenal Regulation with Special Reference to Sweat Glands." The points of view in these chapters, while not identical, agree in stressing the present frontiers of concepts. References are listed after each chapter, *e.g.*, for 7.5 pages on ion transport. An author index and an extensive subject index are provided. Chapter titles at the top of right-hand pages carry chapter numbers, a convenience. The book is gratifyingly free from minor and typographical errors.

The avowed aim of the project is a critical review of "the dynamic and functional aspects of mineral metabolism." Volume I, Part A, clearly stated, readable and authoritative, sets a high standard for the endeavor.

DEPARTMENT OF PHARMACOLOGY UNIVERSITY OF ROCHESTER ROCHESTER 20, N. Y.

HAROLD C. HODGE

Viscoelastic Properties of Polymers. By JOHN D. FERRY, Professor of Chemistry, University of Wisconsin. John Wiley and Sons, Inc., 440 Park Avenue South, New York 16, N. Y. 1961. xx + 482 pp. 15.5 × 23 cm. Price, \$15.00.

Many applications of polymers depend on their viscoelastic properties. Measurements of such properties have long been made and the results used to evaluate different polymeric materials for specific uses. Much of this work has been of a very empirical nature, but in the last decade or two there has been an increasing effort to build a proper scientific background for progress in this field.

A scientist who has been in the forefront in this endeavor is Professor John D. Ferry. He has contributed a great deal to the development of experimental and theoretical techniques for obtaining the maximum degree of knowledge and understanding from experimental measurements in this area. Due in no small part to this work and that of his students, it is now possible to determine the viscoelastic properties of materials over ranges of time, temperature and stress which are much wider than the ranges actually involved in the measurements. With the aid of sound theoretical principles and well-tested generalizations, one can closely relate the macroscopic viscoelastic properties of polymeric materials to molecular characteristics. Many apparently unrelated phenomena can be closely and quantitatively related to each other.

Professor Ferry has now given us a fine, highly unified treatment of this complex field. He deals, not only with elastomers, but also with fibers, crystalline and filled polymers, concentrated solutions, plasticized polymers, gels, etc. Theoretically sound and generally applicable quantitative relationships are emphasized, always with a clear explanation of their significance and how they can be used. It is the reviewer's belief that this book will long remain a standard reference work.

Although the author deals very adequately with the close dependence of viscoelastic properties on molecular flexibility and network formation, he neglects almost completely the relationships between these factors and the chemical composition and structural details of the molecules. This is not said in criticism, but merely to point out that there is