

are well known. Chlorine is known to form hydrogen bonds under favorable circumstances,³ but chlorine compounds analogous to the alkali metal bifluorides have not been reported. We now wish to report the compound $\text{CsCl}\cdot\text{HCl}$, obtained by simply passing hydrogen chloride into rather concentrated aqueous cesium chloride solutions.

In a typical run 2 g. of cesium chloride was dissolved in 1.5 ml. of water and hydrogen chloride was bubbled through the solution with intermittent cooling. As the solution approached saturation with respect to hydrogen chloride, about 1 g. of the new compound was precipitated as colorless to pale yellow anisotropic needles. The solid lost hydrogen chloride and reverted to isotropic cesium chloride when attempts were made to dry it in air or *in vacuo*; but the compound could be obtained with only slight loss of hydrogen chloride when drying was carried out at 30° in a stream of hydrogen chloride. Several samples dried in this way gave ratios $\text{Cs}:\text{H}:\text{Cl}$ varying from 1:0.7:1.4 to 1:1.0:2.0.

Examined in their mother liquors under the polarizing microscope, the crystals were observed⁴ to be perfect orthorhombic prisms, with $2V \sim 70^\circ$, moderately high birefringence, and positive optic sign. As the HCl concentration in the system decreased with time, the needles were transformed first into an anisotropic polycrystalline phase, and eventually into isotropic CsCl .

Cesium appears to be unique among the alkali metals in its tendency to form an "acid chloride." Attempts to prepare similar compounds of rubidium and potassium so far have led only to the normal chlorides. We wish to advance the hypothesis that the new cesium compound contains HCl_2^- anions with a hydrogen-bonded structure ($\text{Cl}-\text{H}\cdots\text{Cl}^-$) analogous to that of the HF_2^- ion; and further, that the HCl_2^- ion forms isolable crystalline salts only with very large cations. Other compounds which may contain the HCl_2^- anion are the "dihydrochlorides" by pyridine and other tertiary amines,⁵ and the remarkably stable siliconium chloride-hydrogen chloride salts.⁶ Structural studies on CsHCl_2 are in progress.

(3) K. Nakamoto, M. Margoshes and R. E. Ruddle, *THIS JOURNAL*, **77**, 6480 (1955); L. R. Zumwalt and R. M. Badger, *J. Chem. Phys.*, **7**, 87 (1939); *THIS JOURNAL*, **62**, 305 (1940).

(4) Preliminary crystallographic examination was carried out with the help of Mr. Terence Patrick of the Department of Geology, University of Wisconsin.

(5) F. Kauffer and E. Kunz, *Ber.*, **42**, 385, 2482 (1909); F. Ephraim, *ibid.*, **47**, 1828 (1914).

(6) W. Dilthey, *Ber.*, **36**, 923 (1903); *Ann.*, **344**, 304 (1906); R. Riley, R. West and W. Erby, unpublished work.

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THE DEGRADATION OF LEUCINE-DERIVED CAROTENES

Sir:

In previous papers on the incorporation of labeled leucine into carotene by *Phycomyces blakesleeanus*, we have shown that only the 4-C of leucine

is incorporated in sufficient quantity to permit its occurrence in each isoprene unit.¹ Incorporation of the 1-C is insignificant, and for the 3-C and 2-C atoms it is too low to account for the increased synthesis of β -carotene in the presence of leucine,² so that the selective use of an intact residual C_5 decarboxylated fragment of leucine becomes untenable.

We have therefore located some of the labeled leucine carbons in the carotene molecule in an attempt to explain the unique role of the 4-C atom.

The labeled carotene specimens, each *ca.* 3.5 mg., diluted with carrier to 19 to 32 mg. were insufficient for a complete analysis such as Grob and Bütler³ performed. They were sufficient for recovery of the acetic acid obtained by chromic acid oxidation,⁴ 6 moles of which are yielded per mole of carotene. The carboxyl groups are derived from the 5,5, 9,9, 13, and 13 carbons, and the methyl groups from corresponding side chains.

The acetic acid was decarboxylated in the Schmidt reaction to give CO_2 and methylamine. The CO_2 was converted to BaCO_3 and counted. The methylamine, crystallized as the hydrochloride, was burned and the CO_2 handled in the same way.

The *dl*-leucine labeled in positions 2, 3 and 4 and the β -carotene were prepared as described previously.^{1,2} At the temperature of boiling water, we oxidized⁵ about 20 mg of β -carotene, from which 3.5 to 5.3 mg. is radioactive.

The acetic acid obtained by four successive distillations was titrated by NaOH , 0.1 *N*. The yield of acetic acid varied from 75 to 85%. The calculated quantities of NaN_3 and H_2SO_4 were added to the CH_3COONa , obtained by evaporation of the solution (42 mg. NaN_3 and 0.9 ml. H_2SO_4 for 40 mg. CH_3COONa).⁶ The liberated CO_2 was collected as BaCO_3 . Then the methylamine was distilled into concd. HCl , crystallized as hydrochloride and burned; the CO_2 was collected as BaCO_3 . The results are tabulated:

Leucine ^a	Total carotene, mg.	Radioactive carotene, mg.	CO_2 c.p.m. ^b per mg. BaCO_3	$\text{CH}_3\text{NH}_2\cdot\text{HCl}$, c.p.m. ^b per mg. BaCO_3
4C	20.1	3.5	298 ± 11.0	4.2 ± 1.1
2C	20.2	3.5	53 ± 7.6	1.6 ± 0.8
3C	32.4	3.5	1.8 ± 0.4	10.1 ± 2.7
3C	19.6	5.3	2.0 ± 0.6	7.2 ± 1.3

^a The counts added to the media differed in each case.

^b The standard deviation was computed to include self-absorption, weighing and counting errors.

The radioactivity of the 4-C is concentrated in the carboxyl group. Thus, the 4-C of leucine is located in positions 5,5, 9,9, 13 and 13 of the carotene molecule.

This strongly suggests that leucine provides an iso C_3 fragment in which the 4-C is centrally located. The distribution for the 2-C of leucine is the same as for the 4-C. Therefore we may assume that a C_2 fragment, also provided by leucine, can

(1) H. Yokoyama, *et al.*, *THIS JOURNAL*, **79**, 2029 (1957)

(2) C. O. Chichester, *et al.*, *J. Biol. Chem.*, **214**, 515 (1955).

(3) E. C. Grob and R. Bütler, *Helv. Chim. Acta*, **39**, 1975 (1956).

(4) E. C. Grob and R. Bütler, *ibid.*, **37**, 1908 (1954).

(5) P. Karrer and A. Helfenstein, *ibid.*, **13**, 1084 (1930).

(6) C. Schuerch and E. H. Huntress, *THIS JOURNAL*, **71**, 2233 (1949).

be incorporated, though to a lesser extent than the C₃ fragment since the total incorporation of activity from the 2-C of leucine is limited.² This is explicable by dilution from a C₂ metabolic pool.

By contrast, the 3-C is found primarily in the methyl of the acetic acid. This does not rule out the possibility that this carbon may also be found

elsewhere in the chain, and several choices still exist as to the pathway followed, which we hope to evaluate when warranted by additional data.

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BOOK REVIEWS

Actions Chimiques et Biologiques des Radiations. Deuxième Serie. I. Les Effets Chimiques Produits par les Rayons Ionisants en Phase Gazeuse. By W. MUND. II. **Phénomènes de Luminescence Provoqués par les Rayonnements de Grande Énergie.** By M. AGENO. III. **Introduction a la Dosimétrie des Radiations.** By N. MILLER. Edited by M. Haissinsky. Masson et Cie. Éditeurs, 120, boulevard Saint-Germain, Paris-6^e, France. 1956. vi + 224 pp. 16.5 × 24.5 cm. Price, Broché, 2,800 fr.; Cartonné toile, 3,400 fr.

This second collection of works consists of related sections on the chemical and physical aspects of ionizing radiations. This series, supplementing the first,¹ deals with the radiation chemistry of gases, with luminescence phenomena and with the dosimetry of ionizing radiations. Each section is written in French by an authority in the field.

The calculation of energy loss by α -particles in gases, the chemical action of low energy electrons and the ionization potentials of simple gases are basic topics treated by Dr. Mund in Part I. Negative ion formation and the methods for differentiating between free radicals and ions in the primary process are also briefly discussed. Mechanisms and some experimental data are given for the radiolysis of inorganic gases such as ammonia, hydrazine, hydrogen sulfide, the halogen acids, ozone, the nitrogen and carbon oxides, and of several organic vapors. Special attention is devoted to the hydrogen-deuterium exchange reaction. Emphasis throughout this section is on the extensive works of Mund and his collaborators. Reaction mechanisms are discussed in terms of free radical reactions and, unfortunately, no assessment is made of the possible contributions of molecule-ion reactions in gas phase radiation chemistry.

Dr. Ageno, in part II, succinctly summarizes the physical aspects of luminescence and compares the effects obtained by ultraviolet light and ionizing radiations. This section of the book is complete and the material is presented in logical order. All phases of luminescence phenomena from the experimental methods, luminescent yields of a large number of substances to the mechanism are covered. Progress in this field is very rapid. As a result, some recent data are missing and some of the older data on mean lives of organic scintillators (Table VI, p. 120) require revision.

Introduction to the Dosimetry of Radiations is an excellent, concise treatment of the physical and chemical methods of dosimetry by Dr. N. Miller in Part III. No attempt is made to describe radiotherapy dosimetry nor the instruments used in dosimetry. The dissipation of energy in matter by charged particles, by electromagnetic radiation and by ionization in gases is outlined. The chapter on relative methods consists of a discussion of several aqueous, organic and luminescent glass dosimeters and of their relative merits. The absolute methods of dosimetry such as calorimetry, charge collection, nuclear reactions in solution and ionization are more completely explained. Useful conversion factors and the oxidation yields of ferrous sulfate for different kinds of radiations are given in the Appendix.

Chemists, physicists, biologists and radiologists interested in the chemical and physical actions of ionizing radiations

will welcome this volume, since material particularly applicable to dosimetry by ionization, scintillation and chemical methods is presented. An English edition will find wide appeal.

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Nouveau Traité de Chimie Minérale. Edited by PAUL PASCAL, Membre de l'Institut, Professeur honoraire a la Sorbonne. Volume X. **Azote—Phosphore.** By R. DUBRISAY and P. PASCAL. Masson et Cie. Éditeurs, Libraires de l'Académie de Médecine, 120 Boulevard Saint-Germain, Paris 6, France. 1956. xxxix + 963 pp. 18 × 25.5 cm. Price, Broché 6,600 fr., Cartonné toile 7,500 fr.

This volume (No. X) is the second to appear of the nineteen volumes projected for the complete treatise. A look around a library's reference shelves discloses that the nitrogen-phosphorus sections of the other large handbooks are now from twenty to thirty years old, which should assure the present treatise a warm welcome. In harmony with the general plan of the treatise, it has been necessary to compress the industrial aspects of the writing in order to make room for the host of new physico-chemical results and interpretations which have developed during the last half-century. A special aid to French readers is afforded by the List of Libraries both Parisian and Provincial (100 in all) in which the relevant Journals may be found, with an indication in each case of the extent to which the available files are complete. Bibliographic references are grouped by tens under general subjects at the end of each section of the book, and most of them purport to cover the literature up to the summer of 1955. At the bottom of each page of text is a reminder of the page where the relevant bibliography can be found. A variety of checks in matters of detail, including comparison with the necessarily much briefer treatments in Yost and Russell's Systematic Inorganic Chemistry (Prentice-Hall, Inc., New York, 1944) indicate that the present volume is in all ways a worthy example of this type of writing—so enormously time-consuming and difficult, and yet so necessary to the progress of science. The material on nitrogen, prepared by the Editor, occupies about 700 pages, while M. Dubrisay has contributed about 215 pages on Phosphorus. In the final chapter (18 pages), M. Pascal returns with a treatment of the organophosphorus compounds. Indexes and other matters bring the total to 963 pages. Printing and make-up are excellent and clear, and the few errors mostly involve minor misreadings of foreign terms in the bibliographies. American users familiar with French will find this a much handier and more selective source of information than Gmelin, though perhaps not quite so complete, when sections of equal date are compared.

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(1) E. J. Hart, *This Journal*, **78**, 2916 (1956).