Notes

mal decomposition of germanic nitride and the direct combination of germanium with nitrogen, were unsuccessful.

The nitride is obtained as a finely divided, dark brown powder, which is slowly hydrolyzed by moisture, when exposed to air, and readily hydrolyzed in solutions of alkali, with the liberation of ammonia. At high temperatures it dissociates to give germanium and nitrogen.

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NOTES

Molecular Changes Accompanying the Radioactive Transformation of Radium D

BY RAYMOND A. MORTENSEN AND PHILIP A. LEIGHTON

The introduction of radioactive elements into volatile organic compounds, for example, radium D tetramethyl into lead tetramethyl, affords an opportunity to investigate molecular changes accompanying radioactive transformations. The expulsion of an electron from the radioactive nucleus of such a molecule not only leaves the molecule an ion, but the resultant recoil of the nucleus as well as its change in atomic number involve relatively large energy changes and raise the question as to whether the molecule is completely decomposed or merely adjusts itself to the new valence conditions.

The transformation of radium D into radium E and then into radium F (polonium) is essentially a change of an atom of lead into bismuth and then polonium. Lead tetramethyl is well known. Bismuth trimethyl has been prepared,¹ and is fairly stable in an inert atmosphere. Diffusion experiments indicate that polonium is bivalent,² and as tellurium forms alkyl derivatives, it is probable that polonium could form a dimethyl compound.

In view of the fact that radium D emits only beta rays which are too feeble to produce an appreciable effect on the electroscope, while radium E and F possess strong beta and alpha activity, respectively, it should be possible by an examination of the vapor above radioactive lead tetramethyl to detect volatile compounds of radium E and F, if present. Lead tetramethyl containing a small amount of radium D tetramethyl was synthesized by means of methylmagnesium bromide from radioactive lead chloride which had been crystallized from a solution of ordinary lead chloride plus a small amount of radium D chloride.

This lead tetramethyl was placed in a small flask and allowed to stand for about thirty days, during which time appreciable quantities of radium E and F were formed. At the end of this period the vapor over the lead tetramethyl was allowed to pass at 25° into a fused silica cell, and was condensed therein at -80° . Up to this point the system was sealed from the atmosphere. The silica cell was then detached from the system, and filled with octane to dissolve the contents. The solution was transferred to a porcelain dish, an excess of bromine added, and the mixture evaporated to dryness in vacuum. The residue was tested immediately, and showed strong initial alpha and beta ray activity, demonstrating the presence in the vapor of volatile compounds of both radium E and F.

Blank experiments indicated that no non-volatile radioactive residue was formed when radium D tetramethyl was allowed to stand for a short time. Exposure of the vapor containing radium D, E and F compounds to ultraviolet radiation (2537 Å.) resulted in the decomposition of all three, the radioactive elements going into a non-volatile residue, which was soluble in nitric acid. An exposure which was sufficient to decompose 99% of the volatile radium E compound decomposed only 22% of the radium D tetramethyl and 7% of the radium F compound.

From the above evidence we must conclude that the radioactive transformation of radium D tetramethyl proceeds entirely to the formation of volatile compounds of radium E and F, presumably radium E (bismuth) trimethyl and polonium dimethyl. This indicates that the molecule of radium D tetramethyl is not completely broken down by the radioactive transformation, but adjusts itself to the new valence conditions by the loss of a methyl group and the completion of the electron pair by the acquisition of an electron from its surroundings, *i. e*.

⁽¹⁾ Schaefer and Hein, Z. anorg. allgem. Chem., 100, 297 (1917).

⁽²⁾ G. v. Hevesy, Physik. Z., 14, 49 (1913).

$$\begin{array}{c} R : RaD: D \longrightarrow R: RaE: + R; \\ R : RaE: RaE: + R; \\ R : RaE: \longrightarrow : RaF: + R \\ R : RaE: \longrightarrow : RaF: + R \\ R \\ \end{array}$$
or
$$\begin{array}{c} RaD(CH_3)_4 \longrightarrow RaE(CH_3)_4^+ + (-) \longrightarrow \\ RaE(CH_3)_3 + CH_3, \text{ etc.} \end{array}$$

This behavior is in marked contrast to the effects of heat and light on the metal alkyls, both of which produce a decomposition into metal and hydrocarbons. While increased vibrational or electronic energy (heat or light) results in the disruption of all of the metal-alkyl bonds, the expulsion of an electron from the nucleus apparently causes the rupture of one bond only.

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x-Ray Patterns of Crystalline Urease and Pepsin

By Isador Fankuchen

Pepsin and urease were studied by means of x-rays, using material prepared by Professor J. B. Sumner. Inasmuch as both materials were obtainable only in the form of microscopic crystals, the powder method alone could be employed. The radiation was from copper and iron targets. The following spacings in Angström units were observed: for urease, 11.2, 4.57, 4.22, 4.15, 3.75, 2.34, 2.13; for pepsin, 49.2, 29.2, 21.0, 15.8, 12.8, 10.7, 9.65, 8.40, 7.16, 4.20, 2.14. With neither pepsin nor urease was there found a strong reflection corresponding to the length of the amino acid residue. It is probable, therefore, that neither substance contains straight chains of amino acid residues. The 4.20 spacing in pepsin was very intense and may correspond to a repetition of a folded amino acid residue chain. In neither case was it possible to make a unit cell size determination. For both pepsin and urease, the same pattern was obtained both from fresh material and from specimens that had lost water and set into a gel. It is probable therefore that the results given here are characteristic only for altered material. The results obtained with pepsin do not agree closely with those of Astbury and Lomax,¹ who state that the chief spacings are 11.5 and 4.6 Å.

(1) Astbury and Lomax, Nature, 133, 795 (1934).

DEPARTMENT OF PHYSICS CORNELL UNIVERSITY ITHACA, NEW YORK

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

Catalysis in the Hydrogen Bromide-Olefins Addition

BY V. N. IPATIEFF, H. PINES AND R. C. WACKHER

It has been shown¹ that the butenes are absorbed by an acetic acid solution of hydrogen bromide while propene under the same experimental conditions is not absorbed. It was thought an analytical method might be developed on this basis for the quantitative determination of propene in a mixture of gases containing butenes.

However, it was found that when a mixture of propene and butenes was passed through hydrogen bromide in glacial acetic acid solution, some of the propene reacted with the hydrogen bromide; the butyl bromide formed promoted the reaction between hydrogen bromide and propene. This led to the study of the effect of other organic compounds upon the speed of addition of hydrogen bromide to propene.

(1) Ipatieff and Dekhanov, J. Russ. Phys.-Chem. Soc., 36, 659 (1904).

Apparatus and Procedure

The gas from an 8-liter glass gasometer was passed through a U drying tube filled with magnesium perchlorate and then through a gas absorber. The absorber was the ordinary gas wash bottle one-third filled with glass beads. It contained the glacial acetic acid solution of hydrogen bromide. Approximately the same quantity of solution was used in each experiment. The gas absorber was surrounded with an ice-bath so as to keep the temperature of the acid solution at 5° . From the gas absorber the gas was passed through a U-tube containing soda lime for absorption of the hydrogen bromide carried over from the reaction flask. The unreacted gas was collected in another 8-liter gasometer. The gas was passed with a speed of 2 liters per hour; readings of the volume of charged gas and exit gas were taken every fifteen minutes. The volumes of gas were computed to standard conditions of temperature and pressure. The alkyl bromides formed were submitted to a fractional distillation.

The apparatus for the experiment with propene and hydrogen bromide gas was smaller but similar to that employed in the other experiments; the pure hydrogen bro-

2398