

able to store, and presumably, therefore, of the relative amounts contained in the previous diet.

Even when the diets devoid of vitamin A were strikingly different in their mineral content and their ability to support the mineral metabolism of the body, the vitamin deficiency of the experimental diet and the vitamin content of the preceding diet together determined the survival period.

The investigation is being continued with reference both to the storage and distribution of vitamin A in the body and the quantitative determination of this vitamin in foods.

NEW YORK, N. Y.

---

### NOTE

**Certain Reactions of Tetryl.**<sup>1</sup>—Next to trinitrotoluene, tetryl or 2,4,6-trinitro-phenylmethyl-nitramine is the most important of the military explosives. At the present time it is probably used by all the great nations as the booster explosive for high explosive shells. Its reactions, then, are not without interest; and mention of its comportment with acids is conspicuously absent from the chemical literature. The vacuum heat test, in which the sample is heated and the evolved gases are collected and measured, is becoming a standard test for tetryl; it is well known that many commercial samples of tetryl contain occluded acid; and a knowledge of the comportment of tetryl with strong sulfuric acid may have considerable bearing upon the interpretation of the heat test.

Mertens<sup>2</sup> observed that when tetryl is heated in various solvents, nitric oxide is evolved and methylpicramide (2,4,6-trinitro-monomethylaniline) is formed. He obtained his best yields by heating tetryl in phenol at 160°, but the product was relatively impure. With aniline, dimethylaniline, glycerol, paraffin and nitrobenzene, he obtained very impure tar-like mixtures. We have verified his results and have found that methylpicramide is produced when tetryl is refluxed in capryl alcohol solution (methylhexylcarbinol) or in *n*-butyl alcohol. With the latter solvent, 46 hours of boiling was required to obtain enough methylpicramide to identify by a mixed melting point. It seems unlikely that tetryl enters into any reaction with those solvents, especially paraffin and nitrobenzene, and the formation of methylpicramide may possibly be due to the action of water fortuitously present or more probably to the action of water and acid produced by the decomposition of another portion of the tetryl.

<sup>1</sup> The experimentation was carried out in connection with a contract between the Ordnance Department and the Massachusetts Institute of Technology, and the present note is published by permission of the Chief of Ordnance.

<sup>2</sup> Mertens, *Ber.*, 19, 2123 (1886).

The result reported by Farmer<sup>3</sup> that tetryl on heating, evolves gas and leaves a residue which contains picric acid and other substances cannot be due to the action of water fortuitously present for Desvergnés<sup>4</sup> obtained picric acid by heating tetryl in a vacuum. Although tetryl is readily hydrolyzed by alkalis to produce picric acid, nitrous acid and methylamine, we find that it is not affected by prolonged boiling with dil. sulfuric acid. Boiled with aqueous chromic acid, however, it yields picric acid, a result which suggests that the formation of picric acid from tetryl in an acid medium is consequent upon oxidation of some kind—and the fused tetryl of Farmer and of Desvergnés was certainly both oxidizing and acid.

Five and four-tenths g. of finely powdered tetryl was refluxed for 46 hours with 100 cc. of water which contained one equivalent of chromic acid in solution. At the end of that time the solution was still reddish-brown. After it had cooled, 2.5 g. of crystals was filtered off and identified as tetryl. The filtrate was extracted first with ethyl acetate and then with ether. On evaporation, the ethyl acetate deposited 2.0 g. and the ether 0.5 g. of picric acid which was identified by a mixed melting point with a known sample.

In another experiment the same quantities of tetryl and of chromic acid were refluxed for seven hours in 50 cc. of glacial acetic acid. The solution turned green, indicating the reduction of the chromic acid. It was poured into 350 cc. of water and on standing deposited 4.4 g. of tetryl. The aqueous solution, made ammoniacal and tested with guanidine nitrate, gave no test for picric acid. In glacial acetic acid, tetryl is destroyed by the oxidizing action of chromic acid and no picric acid is produced.

Tetryl dissolves slowly in concd. sulfuric acid at ordinary temperatures. At 100° it dissolves rapidly with the formation of a red solution. When the solution is poured at once onto cracked ice, the tetryl is reprecipitated. We find that when the solution is allowed to stand for a few days and then poured onto ice, a gummy material precipitates which dissolves readily in warm alcohol and the solution deposits crystals of methylpicramide.

Thirty-five g. of pure tetryl and 100 cc. of c. p. concd. sulfuric acid were introduced into a bottle which was closed with a rubber stopper and allowed to stand at room temperature for 15 days with occasional shaking. The tetryl dissolved fairly rapidly at first, but the last portions went into solution only slowly. The homogeneous liquid was poured onto cracked ice, and a greenish gum precipitated. The aqueous phase gave no test for picric acid, but it gave with the diphenylamine reagent a blue color indicative probably of nitric acid. The gummy material was boiled with alcohol until dissolved, filtered hot, and allowed to cool. The solution became cloudy and an oil separated which crystallized after several days. The solid was purified by dissolving it in the minimum amount of acetone (in which it was very soluble) and adding three volumes of alcohol with rapid stirring. The methylpicramide separated in fine droplets which crystallized promptly, yielding about 6 g. or 20% of that calculated, as yellow crystals, m. p., 111.8°, identified as methylpicramide by a mixed melting point with a sample prepared from picryl chloride and methylamine.

<sup>3</sup> Farmer, *J. Chem. Soc.*, 117, 1603 (1920).

<sup>4</sup> Desvergnés, *Mémorial des Poudres*, 19, 261 (1922).

The reaction is evidently as follows:  $RRN-NO_2 + HOH \rightleftharpoons RRNH + HONO_2$ , the water which is present in the concd. sulfuric acid being effectively involved, and nitric acid being produced. The belief that nitric acid is produced when concd. sulfuric acid acts on tetryl is suggested by the fact that tetryl gives a blue color with the diphenylamine reagent, and is shown to be true by the circumstance reported by Cope and Barab<sup>5</sup> that the nitro group of tetryl (and of certain other nitro-amines such as nitro-urea and nitroguanidine) is quantitatively converted into nitric oxide in the nitrometer. The present reaction then is the reverse of the familiar one in which methylpicramide is nitrated to tetryl.

CONTRIBUTION FROM THE TENNEY L. DAVIS AND CHARLES F. H. ALLEN  
LABORATORY OF ORGANIC CHEMISTRY  
MASSACHUSETTS INSTITUTE OF TECHNOLOGY  
CAMBRIDGE A, MASSACHUSETTS  
RECEIVED FEBRUARY 2, 1924

### NEW BOOKS

**Radioactivity, and the Latest Developments in the Study of the Chemical Elements.**

By K. FAJANS, Professor of Physical Chemistry in the University of Munich.  
Translated from the fourth German edition, by T. S. WHEELER AND W. G. KING.  
E. P. Dutton and Company, 681 Fifth Avenue, New York. xvi + 138 pp. 11 figs.  
22.5 × 14.5 cm. Price \$3.50.

The first edition of Professor Fajans' small monograph was published in the middle of 1919 and immediately received a warm reception. As a worthy member of the excellent "Sammlung Vieweg" it brought up to date the special subject of the influence of radioactivity and the study of nuclear properties on fundamental chemical conceptions, and presented the actual state of the subject in a form readily accessible to all readers with a general scientific equipment. In spite, however, of the simplicity of the presentation, the book was complete, authoritative, and well stocked with references to the literature, so that it filled somewhat the place held by Soddy's "Chemistry of the Radio-elements" a few years earlier. The fourth German edition, of which this book is a translation, brought the subject up to the end of 1921, and the appendix to the present English translation includes references to some work published as late as early 1923. The book is well arranged and interestingly written, and has many good diagrams and plates. The translation is good for the most part, but shows some evidences of lack of clear appreciation of the force of certain German idioms. Professor Fajans is to be congratulated on a fair and even generous exposition of controversial themes and on a wise decision to conform to general usage in the matter of the definition of "element." Fajans had vigorously maintained for years that we must call each isotope a different element, while Paneth and others had explained the value of calling isotopes merely *varieties* of the same element. In this edition the author gracefully bows to the weight of opinion.

NORRIS F. HALL

<sup>5</sup> Cope and Barab, *THIS JOURNAL*, **38**, 2552 (1916).