

ACTION OF RADON ON SOME UNSATURATED HYDROCARBONS

Sir:

In continuing the study of the "Action of Radon on Some Unsaturated Hydrocarbons" [Heisig, *THIS JOURNAL*, **53**, 3245-3263 (1931)] it is found that vinylacetylene condenses to a white solid which becomes orange as the exposure to the action of alpha particles continues. About eleven molecules of the hydrocarbon polymerize per ion pair formed. There is practically no hydrogen and methane evolved.

Propylene condenses to a light mobile liquid. Slightly less hydrogen and methane is given off than in the case of the condensation of ethylene. Somewhat less than three molecules of propylene condense per ion pair formed. The experimental $-M/N$ values agree with those calculated by the method given in the previous paper.

An examination of the heats of formation (from hydrogen and diamond or graphite) of the substance whose action in the presence of radon has been studied shows that the $-M/N$ ratio is higher where the heat of formation is negative and lowest for those substances having a positive or low negative heat of formation.

A calculation of the energy relations using Fajans' atomic linkages [Fajans, *Ber.*, **53**, 643 (1920); **55**, 2836 (1922); *Z. physik. Chem.*, **99**, 395 (1921); Taylor, "Treatise on Physical Chemistry," D. Van Nostrand Co., New York, 1931, p. 323] shows that the condensation of the saturated hydrocarbons is endothermal while that of the unsaturated compounds is exothermal. The exothermal condensations have a higher $-M/N$ ratio than do the endothermal.

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ROTENONE. XVIII. CLEAVAGE OF THE OXIDE RING IN TUBAIC ACID

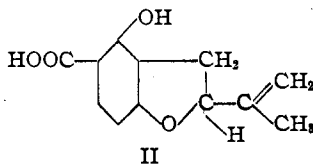
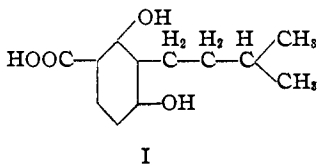
Sir:

It has been shown that tubaic acid ($C_{12}H_{12}O_4$), the only methoxyl-free cleavage product of rotenone thus far obtained, contains a free hydroxyl group, an indifferent oxygen atom and a five-membered side chain. It also contains a double bond, which is easily reduced by catalytic hydrogen to form dihydrotubaic acid. In preparing dihydrotubaic acid it was observed that the amount of hydrogen absorbed was more than the theoretical quantity required for one molecule. Repeated fractional crystallization of the dihydrotubaic acid yielded a small quantity of an acid ($C_{12}H_{16}O_4$) melting at 206° with decomposition. This tetrahydrotubaic acid was found to be practically insoluble in cold chloroform; in alcohol solution it

gave a violet color with ferric chloride, and it was optically inactive. It readily formed a diacetyl derivative, and with dimethyl sulfate and dilute alkali it yielded a monomethoxy methyl ester from which a monomethoxy acid ($C_{13}H_{18}O_4$) was obtained. In alcohol solution this acid also gave a violet color with ferric chloride. Methyl iodide and potassium carbonate failed to methylate the second hydroxyl group of the methoxy acid.

When heated to 210–220° the tetrahydrotubaic acid lost carbon dioxide, and a crystalline phenol ($C_{11}H_{16}O_2$) which melted at 85° was obtained. When treated with aqueous bromine solution, this phenol formed a precipitate and it gave a rose-red color with Guareschi–Lustgarten reagent. With formaldehyde and sulfuric acid it gave a red ring slightly tinged with violet. After fusion with phthalic anhydride and a drop of sulfuric acid, a green fluorescence was obtained on addition of alkali to the dilute solution. Thus the phenol was shown to be an alkyl resorcinol.

The behavior of the acid (insolubility in cold chloroform, color with ferric chloride, and loss of carbon dioxide on heating) indicates that the carboxyl group is ortho to one of the hydroxyl groups and para to the other. The position of the alkyl group, which was indicated by previous work to be an isoamyl group, must therefore be in the 3-, 5- or 6-position ($COOH = 1$). Position 5 is excluded because the phenol (1,3-dihydroxy-4-isoamylbenzene, m. p. 61–62.5°) [A. R. L. Dohme, E. H. Cox and E. Miller, *THIS JOURNAL*, **48**, 1688 (1926)] is known. The alkyl group is probably ortho to one of the hydroxyls because alkyl groups meta to the hydroxyl groups inhibit the fluorescein test [H. Meyer, "Analyse und Konstitutionsermittlung organischer Verbindungen, 5th ed., 1931, p. 321]. Furthermore, the indifference of one of the hydroxyl groups to methylating agents indicates that it is di-ortho substituted. These facts indicate strongly that the substituted resorcinol is 2-isoamylresorcinol. From this and evidence which has been presented previously it follows with a fair degree of certainty that tetrahydrotubaic acid, I, and tubaic acid, II, have the structures



The behavior of tubaic acid on hydrogenation is a significant indication that an analogous process occurs in the case of rotenone and those of its derivatives which yield alkali-soluble products on hydrogenation and that the resulting products are not acids but phenols. It would follow from this assumption that the lactone group is not present in these derivatives.

Further work is in progress upon the tetrahydrotubaic acid and the phenol derived from it.

Experimental proof of the foregoing statements will be presented in detail in an early paper.

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NEW BOOKS

Radiations from Radioactive Substances. By SIR ERNEST RUTHERFORD, O.M., D.Sc., Ph.D., LL.D., F.R.S., JAMES CHADWICK, Ph.D., F.R.S., AND C. D. ELLIS, Ph.D., F.R.S. The Macmillan Company, 60 Fifth Ave., New York, 1930. xii + 588 pp. 138 figs. 16 × 24 cm. Price, \$6.50.

From its appearance in 1913, Rutherford's "Radioactive Substances and Their Radiations" became the English classic of radioactivity. Unfortunately, for the past few years it has been out of print and a new edition has been eagerly awaited. Its place is taken by the present volume, with a change of title and of authorship.

The new title expresses a real change of subject matter. While the earlier work constituted a complete treatise of radioactivity, to have retained the same scope of subject and the same readable style of presentation would have necessitated a book of at least two large volumes. Instead of assuming such an undertaking, the authors elected to limit the present text principally to the nuclear changes and their accompanying radiations.

There are ample reasons to justify this change of policy. The genetic relationships of the radioactive elements and their relationships to the periodic system have not altered greatly since 1913 and may be regarded as a practically completed subject, while the future of radioactivity and the possibility of all evolutionary processes of matter lies in the nucleus. The only possibility of gaining direct information about the highly important structure of the nucleus is by means of the rays and particles which it emits and by its behavior under suitable radiation or bombardment by electrons or alpha particles. It is to the consideration of these topics that the book is devoted with unusual appropriateness, since it was Rutherford who blazed the way to and into the nucleus.

The most recent progress in the structure of the nucleus has been through the application of quantum ideas and of wave mechanics to the energy and wave lengths of the emitted radiations. The interrelationships that have come from the more exact studies of optical and magnetic spectra give indications of a definite and comprehensible nuclear structure. Certainly no co-authors could have been found more competent to write on beta radiation than Dr. Chadwick nor on gamma rays than Dr. Ellis,