at the top of the column. Calculation gives 0.35 g. per day of $N^{15}H_3$, which is consistent with our results.

This run was not entirely satisfactory and is being repeated. We secured better fractionation by the use of lower pressures, the final pressure used being 8 cm. Interruptions occurred due to sediment in the pumps and to repairs to the building steam line. A plot of the results making use of the formula of Huffman and Urey for the rate of attainment of equilibrium in such processes consisted of several parallel lines, breaks occurring at the times of interruption. The slope of the curves indicated that the column should contain approximately 105 theoretical plates for this process, and should produce eventually 50 to 60% N^{15}. The hold-up was especially large, amounting to 1230 g. of ammonia. This is undoubtedly due to the formation of a layer of iron oxide because of corrosion. With this large hold-up the highest concentration could not be expected for a considerable length of time. Toward the end of the run no increased concentration was secured and the run was interrupted. There is thus a discrepancy between the maximum concentration secured and that expected from the formula of Huffman and Urey. This may be due to a breakdown of the formula, but more probably to irregularity in the pumping rates toward the end of the run. Some 130 g. of ammonia was secured by draining the column in batches of 50 to 100 g. of solution. These samples range from 2.54 to 0.80% of N^{15}. The analyses were made with a Bleakney [*Phys. Rev.*, **40,** 496 (1932)] type mass spectrometer. It is possible to analyze for N^{15} within about 0.02%. Due to this sensitivity, the samples of N^{15} obtained are satisfactory for the investigation of chemical and biochemical problems.

We found that the ratios of the isotopes in the original ammonium sulfate and in the gas leaving the top of the column differed by about 5%, giving a simple process fractionation factor of 1.05 instead of 1.027 as reported by Aten and Urey. This seems to be due to the more complete removal of ammonium hydroxide from the solution by the use of low pressures. We have attempted the use of ammonium hydroxide in equilibrium with ammonia to effect a separation of the nitrogen isotopes and have secured a slightly increased concentration of N^{15}. However, the experiments indicate that the simple process fractionation factor in this case is very nearly unity and hence the presence of ammonium hydroxide in the solution should decrease the effective fractionation factor.

CONTRIBUTION FROM
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RECEIVED JUNE 16, 1937

THE SELECTIVITY OF IODIC ACID IN THE OXIDATION OF ORGANIC COMPOUNDS

Sir:

Following work on "oxidation equivalent analysis" [THIS JOURNAL, **59,** 288, 291, 293 (1937)] in this Laboratory, we have made a study of various oxidizing agents hoping to discover some which might be sufficiently selective in their action to make "*partial* oxidation equivalent analysis" a useful tool in determining structure. It was anticipated that determination of the amount of oxidizing agent consumed might yield definite information without making it necessary to isolate oxidation products.

A reagent having these qualifications has been discovered as is evidenced by the striking results given below. The oxidations reported were carried out using mixtures containing 10 ml. of 1% KIO_3 in 40% H_2SO_4, 2 ml. H_2O and 5–6 mg. samples of the organic compounds to be investigated. These were kept at the boiling point of water for one and one-half hours; the iodine liberated was removed by steaming and the unused iodate determined by titration [THIS JOURNAL, **59,** 291 (1937)]. In case no visible iodine liberation took place it was found unnecessary to titrate because such titrations uniformly yielded results comparable with the blanks. All compounds which were oxidized detectably consumed *at least* 4 milliequivalents of oxidizing agent per millimole.

1. All simple aliphatic alcohols tested (up to octyl alcohol) were oxidized *except methanol* which in a sealed tube did not oxidize.

2. Polyhydric alcohols such as glycol, glycerol, erythritol, pentaerythritol, sorbitol, dulcitol, adonitol, mannitol and inositol *failed to be oxidized.* Trimethylene glycol, pinacol and propylene glycol, which have an unoxidized carbon atom alpha to a hydroxyl group, were oxidized.

3. All aliphatic and aromatic aldehydes tested were oxidized.

4. Acetone, methyl ethyl ketone and aceto-

phenone were oxidized. Benzophenone and benzil were not.

5. All simple fatty and aromatic acids including formic, gave negative results. This was true also of glycolic, lactic, tartaric, citric, mucic, mandelic and benzilic acids. All the amino acids of protein origin tested (16 samples) remain unoxidized except cystine, tyrosine and tryptophan. Unsaturated acids, maleic and crotonic, also gave negative results.

6. All aldohexoses tested, glucose, mannose, galactose and their derivatives, α-methylglucoside, pentaacetylglucose, glucosamine, maltose, and lactose failed to be oxidized detectably. Cellobiose and trehalose consumed less than 2 milliequivalents per millimole. This was attributed to impurity.

7. The ketose, fructose and sorbose *were oxidized*, also sucrose (presumably due to fructose formation). Benzoin was untouched.

8. The pentoses, *d*-arabinose and *l*-xylose (and rhamnose, a methyl pentose more slowly) were oxidized, presumably due to furfural formation.

9. Every phenolic compound tested (13 substances) as well as the phenol ethers anisole and phenetole were oxidized.

10. All aniline derivatives tested (7 compounds) were oxidized.

This study is being continued along the lines suggested by the results. We do not, however, expect to go into the specialized field dealing with the structures of sugars where we believe the reagent may be useful.

DEPARTMENT OF CHEMISTRY
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ROGER J. WILLIAMS
M. ALLAN WOODS

RECEIVED JUNE 7, 1937

NEW BOOKS

The Organic Chemistry of Nitrogen. By N. V. SIDGWICK, F.R.S. New edition, revised and rewritten by T. W. J. TAYLOR, M.A., Oxford, and WILSON BAKER, M.A., D.Sc., Oxford. Oxford University Press, 114 Fifth Avenue, New York, N. Y., 1937. xix + 590 pp. 17 × 25.5 cm. Price, $8.50.

Since the appearance of the original edition of this book in 1910 theoretical chemistry has advanced at a whirlwind pace. The past quarter of a century has seen the introduction of the atomic theories of Bohr and Lewis and finally of the wave mechanics as an integral part of theoretical chemistry. In the description of chemical phenomena in these terms the chemist has been aided by dipole moment measurements, absorption spectra, Raman spectra and electron diffraction measurements. The revision of Professor Sidgwick's famous book has been carried out ably in terms of these new concepts and the related experimental evidence.

The chapter headings are: I. Esters of Hyponitrous, Nitrous, and Nitric Acids; II. Aliphatic Amines; III. Aromatic Amines; IV. Amino Acids; V. Amides; VI. Hydroxylamine Derivatives; VII. Nitroso Compounds; VIII. Nitro Compounds; IX. Carbonic Acid Derivatives; X. Derivatives of Cyanogen; XI. Aliphatic Diazo Compounds and Derivatives of Hydrozoic Acid; XII. Hydrazine Derivatives; XIII. Aromatic Diazo Compounds; XIV. Azoxy and Azo Compounds and Other Compounds Containing Two Linked Nitrogen Atoms; XV. Compounds Containing a Chain of Three or More Nitrogen Atoms; XVI. Cyclic Polymethylene-Imines (Excluding Pyrrolidine and Piperidine); XVII. Five-Membered Rings; XVIII. Six-Membered Rings.

In the chapter on amines the structure of the quaternary ammonium salts is given as involving four covalences and an electrovalence. The weak basicity of the primary, secondary and tertiary amines is explained in terms of the hydrogen bond.

Under the heading of aromatic amines is the first application of the idea of resonance-hybrids. There are three possible structures of the positive ion of the triphenylmethane dyes differing only as to which of the rings has quinoid structure. The actual state of the ion is a hybrid between all three and to this fact are related the properties of the substance as a dye. This concept has been logically applied to all the classes of dyes discussed throughout.

The fourth chapter gives a full discussion of the amphoteric properties of the amino acids from a modern physicochemical point of view. The various equilibria involving the zwitterion are fully discussed and the data on the acidic and basic dissociation constants correlated from this point of view.

Along with the hydroxylamine derivatives the interesting free radicals $R_2N{\rightarrow}O$ are discussed and attention drawn to the magnetic properties produced by the unpaired electron. There is a very full discussion of the evidence concerning the configuration of oximes and the effect of