

It now appears that Professor Chichibabin did not as a matter of fact report the diazotate reaction as a method for the preparation of alpha-phenoxy pyridine, its isolation being merely incidental in the reaction which he was investigating. Unfortunately, we had only abstracts of the Russian article at our disposal.

The designation of 2-phenoxy pyridine as the only alpha-substituted pyridine reported in the literature (page 297) is a very patent error, since a large number of alpha-substituted pyridines have been known for many years and the writer had dealt with derivatives of such compounds in two earlier publications, as well as in the paper under discussion. (Note reference to Grave's article page 298.) On examination it was found that this error was due to the accidental omission of *aryloxy-* after *alpha-* in the term "alpha-substituted pyridine," in the final typing of the manuscript.

NEW YORK UNIVERSITY  
NEW YORK CITY

R. R. RENSHAW

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#### FLUOROCARBONS

Sir:

From a reaction mixture of carbon and fluorine the following fluorocarbons have been isolated and identified by their molecular weights: profluorane,  $C_3F_8$ ; bufluorane,  $C_4F_{10}$ ; pentafluorane,  $C_5F_{12}$ ; and hexfluorane,  $C_6F_{14}$ . The well-known compounds methfluorane,  $CF_4$ , and ethfluorane,  $C_2F_6$ , were also formed in the reaction. The separation was made by distillation and the molecular weights were determined with an all-glass density balance. Seven to fifteen grams of each compound was obtained. The boiling and freezing points have been determined approximately and are: profluorane f. p.  $-183^\circ$ , b. p.  $-36^\circ$ ; bufluorane f. p.  $-84.5^\circ$ , b. p.  $+4^\circ$ ; pentafluorane f. p.  $-10^\circ$ , b. p.  $+30^\circ$ ; and hexfluorane f. p.  $-4^\circ$ , b. p.  $+60^\circ$ .

The distillation was performed in a low temperature column packed with glass helices. It was carried out at 200 mm. and the temperature remained constant within  $1^\circ$  during the collection of each fraction. The molecular weights as obtained from the density balance and determined at short intervals during the distillation remained constant so long as the temperature remained constant. Each fraction was redistilled and the same molecular weights obtained:  $C_3F_8$  184,

188;  $C_4F_{10}$  234, 238;  $C_5F_{12}$  277, 288; and  $C_6F_{14}$  328, 338. The precision of the density balance decreased as the molecular weight increased, and the increased adsorption of the higher boiling substances resulted in low values. The balance was calibrated with oxygen and carbon dioxide and was checked with  $CF_4$  and  $C_2F_6$ , which gave the theoretical values of 88 and 138. The redistilled fractions had relatively sharp melting points when observed visually.

The existence of these compounds has been previously postulated from the properties of small quantities of mixtures of fluorocarbons [Ruff and Keim, *Z. anorg. allgem. Chem.*, **192**, 249 (1930); Ruff and Bretschneider, *ibid.*, **210**, 173 (1933); **217**, 1 (1934); **217**, 19 (1934)]. Their separation and individual identification however, has not been reported previously. A greater quantity will be made and the chemical and physical properties determined.

POND CHEMICAL LABORATORY  
PENNSYLVANIA STATE COLLEGE  
STATE COLLEGE, PENNSYLVANIA

J. H. SIMONS  
L. P. BLOCK

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#### A CONCENTRATION OF $N^{15}$ BY A CHEMICAL EXCHANGE REACTION

Sir:

Using the exchange reaction between ammonia gas and ammonium sulfate solution suggested by Urey and Greiff [THIS JOURNAL **57**, 321 (1935)] and investigated by Aten and Urey [*Phys. Rev.*, **50**, 575 (1936)] and using the apparatus devised by Huffman and Urey [*Ind. Eng. Chem.*, **29**, 531 (1937)] we have attempted to concentrate the heavy isotope of nitrogen for use in biochemical and chemical investigations. The method consists of pumping a 30% solution of ammonium sulfate at a constant rate of 15 cc. per minute into the top of the fractionation column under low pressure, liberating the ammonia from the salt in solution at the bottom by the addition of sodium hydroxide and stripping the ammonia from the solution by a packed stripping column. This ammonia was fed back to the bottom of the column and escaped from the top. As the result of a thirteen-day run of this kind we have produced nitrogen containing 2.54% of  $N^{15}$ , a  $6\frac{1}{2}$  fold increase in concentration.

The transport of heavy ammonia is equal to the total flow multiplied by the difference in concentration of heavy ammonia in the solution and gas

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  
DEPARTMENT OF CHEMISTRY  
COLUMBIA UNIVERSITY  
NEW YORK, N. Y.

H. C. UREY  
MARVIN FOX  
J. R. HUFFMAN  
H. G. THODE

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#### 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-