

These and other results demonstrate the close relationship of nicotinic acid and the amide to black tongue. The fact that nicotinic acid amide is an essential ingredient of the diet is not surprising since it is a component of certain coenzymes. However, the observation that a deficiency of this material may be the cause of black tongue is most interesting. Whether these compounds are equally effective in human pellagra can only be answered by clinical trials.

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A WATER-SOLUBLE LIGNIN SULFONIC ACID FROM AN EXTRACTED OAK LIGNIN

Sir:

The authors have succeeded in preparing a water-soluble lignin sulfonic acid from an *extracted* lignin by the following method: solvent-extracted, oak wood meal was acetylated by a modification of the method of Suida and Titsch [*Monatsh.*, **54**, 700 (1929)] and the isolated, acetylated lignin-carbohydrate complex hydrolyzed in cold aqueous acetone solution with sodium hydroxide. Filtration and acidification of the filtrate gave an oak lignin which could be separated into two fractions: (a) a chloroform-soluble (10%), and (b) a chloroform-insoluble fraction (90%). *Anal.* (a) OCH₃, 23.4%; (b) C, 63.9; H, 6.2; OCH₃, 20.6. The fully methylated lignins showed C, 65.2; H, 6.8; OCH₃, 37.6. The oak lignin was readily and completely soluble in sodium bisulfite cooking liquor at 100–125°. Treatment of the lignin sulfonic acid (OCH₃, 23.0) (collaboration of W. L. Hawkins) with alkali yielded a mixture of equal parts of vanillin and syringic aldehyde (total yield 4.6%). Its properties, as well as those of the lignin from which it is derived, are now being investigated thoroughly on account of the importance of such data for use in studies on the mechanism of sulfite pulp manufacture.

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THE NITROGEN ISOTOPE (N¹⁵) AS A TOOL IN THE STUDY OF THE INTERMEDIARY METABOLISM OF NITROGENOUS COMPOUNDS

Sir:

Urey, Fox, Huffman and Thode [THIS JOURNAL, **59**, 1407 (1937)] have recently succeeded in concentrating the nitrogen isotope of atomic weight 15 (N¹⁵). Professor Urey has kindly supplied us with a sample of ammonia enriched in N¹⁵. It had a N¹⁴/N¹⁵ ratio of 160 as compared to a normal of 266. All isotope analyses were carried out with a mass spectrometer. Glycine and hippuric acid were synthesized from this ammonia.

For metabolism studies of organic compounds with isotopes it is essential that the labelled atom be stable and not exchange with the same element of other compounds. We have studied the systems glycine-ammonia, hippuric acid-ammonia, hippuric acid-glycine, and tyrosine-glycine, and have found no exchange of the nitrogen.

Two groups of experiments on biological hippuric acid formation were carried out on rats with the new compounds. The urinary hippuric acid, after either feeding or injection of hippuric acid (N¹⁵), contained a mixture of about one-third normal acid and two-thirds of the material fed. When glycine and benzoic acid were given together by the same methods, the urinary hippuric acid contained about two-thirds normal hippuric acid and one-third hippuric acid (N¹⁵).

The experiments indicate that hippuric acid can be absorbed from the intestinal tract without being hydrolyzed, and furthermore suggest that glycine may be directly utilized for hippuric acid formation. The nitrogen isotope should prove to be as useful in the study of the intermediary metabolism of nitrogenous compounds as deuterium is in the study of fat and sterols.

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CATALYTIC ISOMERIZATION OF *n*-BUTANE AND ISOBUTANE

Sir:

Glasebrook, Phillips and Lovell have recently reported [THIS JOURNAL, **58**, 1944 (1936)] a low temperature, catalytic isomerization of *n*-pentane to isopentane in the presence of aluminum halides.

The reaction was accompanied in its later stages by simultaneous catalytic cracking with formation of large amounts of isobutane and deposition of a typical aluminum halide lower layer. No attempt was made to study the reverse isomerization.

It has been found that in the case of the butanes under similar conditions a reversible isomerization takes place uncomplicated by cracking so that fairly accurate values of the equilibrium constant of the reaction



may be experimentally determined.

The reactions were carried out at room temperature in the liquid phase under the equilibrium vapor pressure of the butane mixture (40–50 lb. per sq. in.) (3 atm.). Stainless steel pressure bombs were used with a suitable rocking attachment to ensure thorough agitation. Anhydrous aluminum bromide was found to be an effective catalyst and was usually employed in 5 mole per cent. concentration, experiment having shown that the equilibrium composition was unaffected by change in catalyst concentration. The course of the reaction was followed by analysis of gas samples from the bombs. For this purpose an automatic recording microfractionation column was used. The composition of the liquid phase was calculated from the gas analyses by assuming validity of Raoult's law and correcting for the dissolved aluminum bromide. The method of calculation was checked at the end of each experiment by direct analysis of the liquid phase when no further change was observed in several successive gas samples. Agreement between directly analyzed and calculated liquid phase composition was always within 3%.

The equilibrium mixture of butanes in the liquid phase at room temperature (about 27°) consists of 78–82 mole per cent. of isobutane and 18–22 mole per cent. of *n*-butane. The equilibrium has

been approached from both sides and experiments have been carried out on the *c. p.* butanes separately as well as on butane mixtures of known composition. The reactions are quite slow, over two months being required to reach equilibrium at room temperature starting with the pure compounds and 5 mole per cent. of catalyst. No detectable amounts of hydrocarbons other than the butanes have been found in the liquid phase at equilibrium although traces (2–3%) of lower paraffins, principally methane and ethane, are usually found in the gas samples. The amount of lower paraffins present is practically constant throughout the reaction. At the end of two months the aluminum bromide can be recovered apparently unchanged. No tarry layer of unsaturated halide complex, usually characteristic of aluminum halide reactions, has ever been observed.

The results indicate that the difference in thermodynamic stability of isobutane and *n*-butane at room temperature is somewhat greater than that predicted from the approximate statistical calculations of Pitzer [*J. Chem. Phys.*, **5**, 473 (1937)] and Kassel [*ibid.*, **4**, 276 (1936)] and probably differs in sign from that predicted from the entropy measurements of Parks, Shomate, Kennedy and Crawford [*ibid.*, **5**, 359 (1937)].

The kinetics of the isomerization reactions and the effect of temperature on the equilibrium composition will be reported in a forthcoming article. The method of catalytic isomerization under such conditions that reaction takes place slowly with no undesirable cracking will, it is hoped, afford a means of determining equilibrium constants in other paraffin isomerization reactions.

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