ratus or management, but would prefer the rotary still and the continuous process.

With regard to the other step wherein the acetone is converted into chforoform, this is accomplished by a reaction that was long and well known before the date of the patent, and the proper portions of the material required for the reaction were easily obtainable by calculation, and this knowledge also ante-dated the patent. The patent then simply covers a specially devised and described apparatus and management which the writer does not use and does not want to use even if they were not patented, but much prefers his old form of apparatus and management described in 1857, and used for many years in making alcohol chloroform. And the successful use of this apparatus and management for acetone chloroform is simply in accordance with the statement of Liebig, in 1832, that acetone could be successfully used under the same conditions as alcohol.

PYRIDINE ALKYL HYDROXIDES.[1]

BY A. B. PRESCOTT AND S. H. BAER.

Received January 27, 1896.

THE HYDROXIDES OF QUATERNARY NITROGEN BASES IN GENERAL.

TETRAMETHYL and tetraethyl ammonium hydroxides were well described by their discoverer, A.W. Hofmann,[2] in 1851. Their crystallization in a vacuum, their behavior as alkalies in reaction with the metallic salts, and their conversion to carbonates upon exposure to the air were then set forth. Various quaterary bases of mixed formation from methyl, ethyl, amyl and phenyl were made by Hofmann at the same time. The tetrapropyl ammonium hydroxide was first described by Roemer, in 1873.[3]

The decomposition of quaternary ammonium hydroxides by heat was reported upon by A. W. Hoffmann, in 1881,[4] also by Lawson and Collie, in 1888.[5]

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[1] Read at the Cleveland meeting.

[2] Phil. Trans., *1851*, (2), 357; *Ann. Chem.* (Liebig), **81**, 253, **86**, 292, **91**, 33.

[3] H. Roemer, *Ber. d. chem. Ges.*, **6**, 786.

[4] *Ber. d. chem. Ges.*, **14**, 494.

[5] *J. Chem. Soc.*, **53**, 634.

Pyridine ethyl hydroxide was mentioned by Anderson in 1855.[1] The methyl hydroxide was reported upon by A. W. Hofmann in 1881.[2] In this relation are to be considered the numerous products of the action of alkalies upon the alkyl iodides of pyridine and quinoline, obtained by Claus and by Decker, mostly in 1892 and 1893.[3]

PYRIDINE PROPYL HYDROXIDE.

Pyridine propyl iodide, prepared as stated in another paper from this laboratory,[4] was treated with moist recent silver oxide, shaking for some time in a flask, keeping down the temperature. The silver oxide for all this work was made by precipitating silver nitrate with potassium hydroxide and washing the precipitate until the washings give no color reaction with hematoxylin, to ensure the removal of the alkali. Silver oxide is sufficiently soluble in water for its solution to color litmus or phenolphthalein.

On filtering out the silver iodide, the solution of pyridine propyl hydroxide was colorless, and was found to precipitate salts of lead, silver, copper, iron, aluminum, chromium, cobalt, and nickel, an excess of the hydroxide dissolving only the precipitates of lead and of aluminum, these reactions agreeing with those of fixed alkalies. In parallel treatment with pyridine it was found not to precipitate these salts, the only apparent reaction with any of them being a blue color with the copper salt. The solution of pyridine propyl hydroxide gave the alkaline reaction with the following indicators: litmus, phenolphthalein, brazil wood, cochineal, hematoxylin, and methyl orange. Pyridine gives an alkaline reaction with all these indicators except phenolphthalein and hematoxylin, these two being capable of use in a volumetric acid estimation of the pyridine propyl hydroxide in presence of pyridine.

On heating the solution of the pyridine propyl hydroxide it acquires a red color, and the solid residue by evaporation has a black color, dissolving in water again as a red solution.

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[1] *Ann. Chem.* (Liebig), **94**, 361.

[2] *Ber. d. chem. Ges.*, **14**, 1498.

[3] *J. prakt. Chem.* (2), **46**, 106, **47**, 208, 426; *Ber. d. chem. Ges.*, **25**, 3326.

[4] A. B. Prescott, this Journal, **18**, 92.

PYRIDINE ISOPROPYL HYDROXIDE.

This base was prepared in the same manner as the normal propyl hydroxide, and it was found to give the same reactions with indicators and with metallic salts, as well as the same color when evaporated.

The isopropyl[1] base has been elsewhere stated by one of us to form a more stable iodide, of higher melting point and lower solubilities, than the iodide of the normal propyl base, and the isopropyl hydroxide has been taken, instead of the normal propyl hydroxide, in our further experimentation.

The production of the pyridine isopropyl hydroxide, in solution, can be made quantitatively complete as a base saturating sulphuric acid. Weighed portions of the iodide were converted to hydroxide in solution, with due precautions against loss, and the liquid titrated with tenth normal solution of sulphuric acid, using hematoxylin and cochineal, respectively, as indicators, and titrating back to the end reaction with tenth normal solution of potassium hydroxide. The hematoxylin was used in a titration to avoid interference by free pyridine, should this be present as a product of decomposition, as it does not color this indicator. The cochineal was used because it is an indicator of special delicacy for titration of pyridine alkyl hydroxides.

The results were as follows: the percentage of hydroxide *calculated* from the iodide being 55.82, the percentage of hydroxide *found* by titration with cochineal was 55.25 and 55.88, with hematoxylin it was 55.6 and 55.7.

The solution of pyridine isopropyl hydroxide, on evaporation to dryness, yields a black residue, which is permanent, so that after standing three months it gives with metallic salts all the reactions of the hydroxide. The color in solution changes to red, like that of the normal propyl hydroxide. By exposure to the air it is steadily converted to the carbonate.

When the solution was treated for some time with carbon dioxide gas, then evaporated to dryness, the residue was found to bear the composition of a normal carbonate of the univalent base. This composition was determined from the amount

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[1] Pyridine Alkyl Iodides, this Journal, 18, 93.

of carbon dioxide recovered in an absorption train, in ratio to the weight of iodide taken for conversion to hydroxide. The calculated weight of carbon dioxide being 14.44 per cent. of $(C_5H_5N.C_3H_7)_2CO_3$, there were obtained 14.99. 14.88, and 14.79 per cent. of carbon dioxide. In other trials the carbonation was incomplete, reaching only to 9.3, 9.47, and 10.1 per cent.

In no case was the full quantity of pyridine isopropyl hydroxide obtained in weight of the dry residue, although the evaporation was conducted under different conditions, in vacuum, in a stream of dry air, and in a stream of dry hydrogen. In the case of the carbonate, the weight of the residue did not fall below the theoretical quantity. As hydroxide the weight of the residue always fell a good deal short of the full quantity.

Pyridine isopropyl platinum chloride, perfect in proportions, was prepared from the black residue left on evaporation of the water solution of pyridine isopropyl hydroxide, by treatment in the usual manner. The black mass was dissolved in alcohol, treated with hydrochloric acid and platinum tetrachloride, and the crystalline precipitate fitted for analysis. Fine crystals were obtained, not melting below temperatures which cause decomposition.

	Calculated for $(C_5H_5N.C_3H_7Cl)_2PtCl_4$.	Found. I.	II.	III.
Platinum	29.95	30.08	30.48	30.29
Chlorine	32.58	32.50	....	32.39
Ratio of Cl to Pt	100:108	100:108	....	100:107

Pyridine isopropyl sulphate, the normal salt, was also prepared in fine crystals, by adding sulphuric acid to the hydroxide.

In various efforts to obtain the pure hydroxide in the solid state, crystalline or amorphous, vacuum desiccation, freezing temperatures, formation in absolute alcohol solution, and other agencies were successively tried, without success. Crystals were not obtained, and the residue was always dark colored. Evaporation in a stream of dry hydrogen yielded a residue of the same weight as that obtained by evaporation in a stream of dry air.

These results, so far, may be summarized as follows :

Pyridine isopropyl hydroxide remains in aqueous solution tor a time without decomposition or loss in any way. The residue by evaporation of this solution, in air, or hydrogen, or vacuum, contains a considerable portion of the unchanged hydroxide, along with certain decomposition products not yet determined. The normal carbonate of this base, its normal sulphate, and its platinum chloride are easily prepared and preserved.

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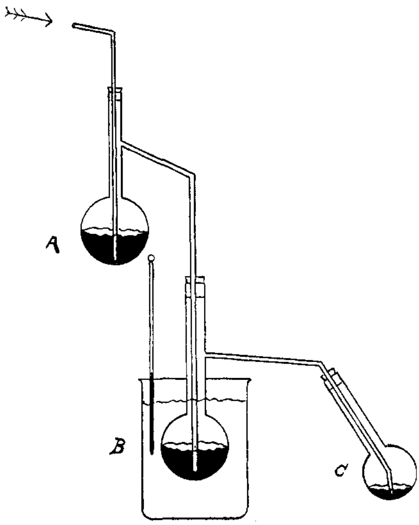
ON THE REDUCTION OF SULPHURIC ACID BY COPPER, AS A FUNCTION OF THE TEMPERATURE.[1]

BY LAUNCELOT ANDREWS.

Received January 9, 1896.

THE object of the experiments described in this paper was to determine whether the reduction of sulphuric to sulphurous acid by copper take place at a higher or a lower temperature than the incipient dissociation of the former compound into water and the acid anhydride.



The sulphuric acid employed was the ordinary pure product, containing 98.4 per cent. of sulphuric acid. The apparatus illustrated in the adjoining figure was used.

The method resorted to was to heat the copper with the sulphuric acid (in flask *B*) gradually in a sulphuric acid bath, while passing a dry current of air or of carbon dioxide through it. The escaping gas was then tested (in flask *C*) by suitable reagents, to be described, for sulphuric and sulphurous acids respectively. Flask A contained concentrated sulphuric acid at the ordinary temperature (25° C.) to dry the gas, which was passed at the rate of about eighty bubbles per minute, except when otherwise men-

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[1] Read before the Iowa Academy of Sciences, January 2, 1896.