Proceedings of the Iowa Academy of Science

Volume 48 | Annual Issue

Article 48

1941

Effects of Hydrogen Ion Concentration upon the Hydrolysis Rates of Ketimines (Abstract)

I. Johnson

Cornell College

J. B. Culbertson Cornell College

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Recommended Citation

Johnson, I. and Culbertson, J. B. (1941) "Effects of Hydrogen Ion Concentration upon the Hydrolysis Rates of Ketimines (Abstract)," *Proceedings of the Iowa Academy of Science, 48(1),* 247-248. Available at: https://scholarworks.uni.edu/pias/vol48/iss1/48

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and "dicalite" as an adsorbent the following separations have also been made: lactose and galactose, sucrose and d-d-glucose, trehalose and B-d-glucose.

IOWA CITY, IOWA.

EFFECT OF HYDROGEN ION CONCENTRATION UPON THE HYDROLYSIS RATES OF KETIMINES

(ABSTRACT)

I. JOHNSON AND J. B. CULBERTSON

Measurements have been made upon the hydrolysis rates of ketimine hydrochlorides to obtain information concerning the relation between their varied structures and stability toward hydrolysis.1 The hydrogen ion concentration might appear as a catalytic factor in this hydrolysis.² It would thus seem necessary to determine these hydrolysis rates at the same hydrogen ion concentration if this factor has a marked effect. Different ketimine hydrochlorides alone in water produce, in the dilute solutions usually employed, pH values ranging initially from about 3.6 to 5.3 and increasing in each case toward the pH of the equivalent ammonium chloride formed as the result of hydrolysis. Certain measurements on the hydrolysis rates of ketimine hydrochlorides of widely different initial pH values in water, to which an equivalent of hydrochloric acid was added, showed that their speed was actually lowered by this hydrogen ion increase although not enough to affect the general order of the rate.

In the studies for this report the hydrolysis rates for two ketimine hydrochlorides, representing extremes in initial hydrogen ion concentration of their hydrolyzing solutions, have each been measured in buffered solutions at several pH values ranging from 2 to 5. The results reveal a decrease in rate of hydrolysis with increase of hydrogen ion concentration, although the effect is not sufficient to markedly affect the general comparative order of the velocity constants of various ketimine salts.

Without making any attempt to analyze more critically the role of hydrogen ion concentration upon the hydrolysis rate of ketimine salts at this time, we may conclude that hydrolysis velocity measurements made upon the simple unbuffered ketimine salts

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may be used in comparisons involving the far stronger effects due to structural differences.

(1) Proc. Ia. Acad. Sc. 38, 169-70 (1931); 40, 113 (1933); 41, 172 (1934).

(2) Stieglitz, Am. Chem. J., 39, 31 (1908).

CORNELL COLLEGE, Mt. Vernon, Iowa.

ACTION OF THIONYL CHLORIDE ON URETHANES (ABSTRACT)

H. B. FREYERMUTH AND L. CHAS. RAIFORD

Raiford and Shelton [J. Org. Chem., 4, 207 (1939)] found that hot pyridine causes 2-carbophenoxyamino-4-methyl-6-bromophenyl p-tolylsulfonate to lose phenol and give a "condensation product" which was found to be a 1,3- derivative of uretedione (uretidone). This type of derivative was also obtained by Warren and Wilson [Ber., 68, 957 (1935)] by the action of thionyl chloride on phenylurethane. But it has now been found that the last-named reaction is specific for phenylure thane. When the phenyl radical contains a "negative" substituent, thionyl chloride causes no action after five hours refluxing. If the substituent is alkyl the treatment causes tar formation, from which nothing definite could be isolated.

Ethyl and n-butyl carbamates react with thionyl chloride to give the corresponding esters of allophanic acid and small amounts of cyanuric acid. Under the same treatment 2-naphthylurethane undergoes chlorination to give the 1-chloro derivative, while the 1-naphthyl compound gives the 4-chloro derivative.

LABORATORY OF ORGANIC CHEMISTRY, STATE UNIVERSITY OF IOWA. IOWA CITY, IOWA.

THE ACTION OF THE ETHANOLAMINES ON CORNSTALK LIGNIN

(Abstract)

ELTON FISHER

A previous paper has shown that the amount of lignin removed from plant tissue by organic nitrogen bases is dependent on the basic strength of the extracting agent. It was also shown that these bases form nitrogenous compounds with lignin.