methyl alcohol or formaldehyde, which are possible intermediate compounds in the more favored reaction of producing methane. The hydrogenation of the ethylene is prevented by the poisoning effect of carbon monoxide on the metal surface adjoining.

From these results we conclude that small amounts of ethylene can be formed by the catalytic reduction of carbon monoxide under special conditions. Owing to the small amounts produced, the short life of the catalyst, and the difficulty of securing consistent results, the commercial production of this substance does not seem feasible at atmospheric pressure.

Summary

A mixture of approximately equal parts of carbon monoxide and hydrogen with a trace of oxygen, when passed at a space velocity of from 1500 to 2000 over a nickel-palladium catalyst supported on aluminum or pumice stone, produced from 1 to 3% of ethylene at temperatures in the neighborhood of 100°. The catalyst lost one-half of its efficiency in 30 hours.

Other catalysts in order of decreasing activity were nickel-copper-palladium, iron-nickel-palladium, nickel-platinum, copper-cobalt-iron, copper-palladium, copper-cobalt-nickel, carbon-palladium, nickel-copper, copper-cobalt.

While saturated hydrocarbons were not especially sought, nickel and nickel-palladium catalysts yielded from 20 to 25% of methane at temperatures in the neighborhood of 250°. The catalysts showed little decrease in activity after several days' use.

MIDDLETOWN, CONNECTICUT

[CONTRIBUTION FROM THE SECTION ON PHYSICS OF THE MAYO CLINIC AND THE DIVISION OF EXPERIMENTAL SURGERY AND PATHOLOGY OF THE MAYO FOUNDATION]

THE CATALYTIC AND SPECIFIC DYNAMIC ACTIONS OF CERTAIN AMINO ACIDS[1]

BY JOHN M. ORT AND JESSE L. BOLLMAN

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Introduction

The lack of any generally accepted explanation for the differences in the actions of the various amino acids in promoting oxidation in the animal organism suggested further investigation of the effects of these compounds on oxidation *in vitro*. Using the method of oxidation potentials developed by Clark[2] and his associates, we have studied the action of hydrogen

[1] Read before the American Chemical Society, Philadelphia, Pennsylvania, September 6–11, 1926.

[2] Clark, Cohen, Sullivan and Gibbs, *U. S. Pub. Health Repts.*, **38**, 443, 666, 933, 1669 (1923); **39**, 381, 804 (1924); **40**, 649, 1131 (1925); *U. S. Pub. Health Repts., Suppl.*, No. 54, 55.

peroxide on dextrose, both in the presence and absence of several amino acids. By this method we were able to have at all times an instantaneous indication of the oxidation or reduction tendencies in the solutions under observation without any exposure to the air or without removal of any of the solution for chemical analysis. The apparatus and experimental procedure are modifications of Clark's and have been described elsewhere.[3]

The negative potentials of alkaline dextrose were instantly changed to more positive potentials by the addition of hydrogen peroxide. Then, if the hydrogen peroxide reacted, the potentials were observed to drift back to more negative values; if not, the potentials remained positive for a six-hour period. The hydrogen-ion concentration was accurately held at a P_H of 10.00 ± 0.01. Hydrogen-electrode measurements were made on

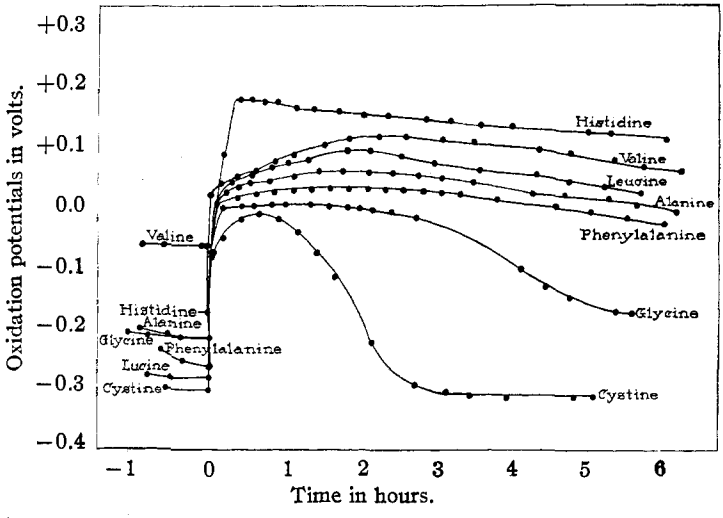

Fig. 1.—Amino acids with catalytic action; 0.5 cc. of 0.03% H_2O_2 added at time zero.

exactly the same buffered solutions as were used for the oxidation-potential measurements. One hundred cc. of a mixture of 0.1 *N* sodium hydroxide and 0.067 *M* disodium phosphate solutions was used as the buffer in all cases. In this solution, except where otherwise specified, 0.001 mole of amino acid and 200 mg. of dextrose were dissolved. The temperature was kept constant at 30° ± 0.02°.

Results of Experiments

It was found (Fig. 1) that when both dextrose and any one of seven of the amino acids studied were present, a drift of potential from the positive oxidizing values acquired just after the addition of hydrogen peroxide

[3] Ort, *J. Optical Soc. Am.*, **13**, 603 (1926).

toward more negative or reducing potentials would begin to take place within about two hours after the addition of the hydrogen peroxide. These seven amino acids are alanine, phenylalanine, leucine, histidine, valine, glycine and cystine. When either dextrose or the amino acid (except in the case of cystine) was absent, this drift was also absent. The potentials showed no drop from the oxidizing values during the six hours of study (Fig. 2). Hence the action involves all three, dextrose, amino acid and hydrogen peroxide. Cystine with its sulfur groupings is certainly entirely different from any of the other amino acids studied. It belongs to the reversible oxidation-reduction systems reported by Kendall and Nord.[4] Yet its drop after the peak is reached has been found to be much less rapid when dextrose is absent.

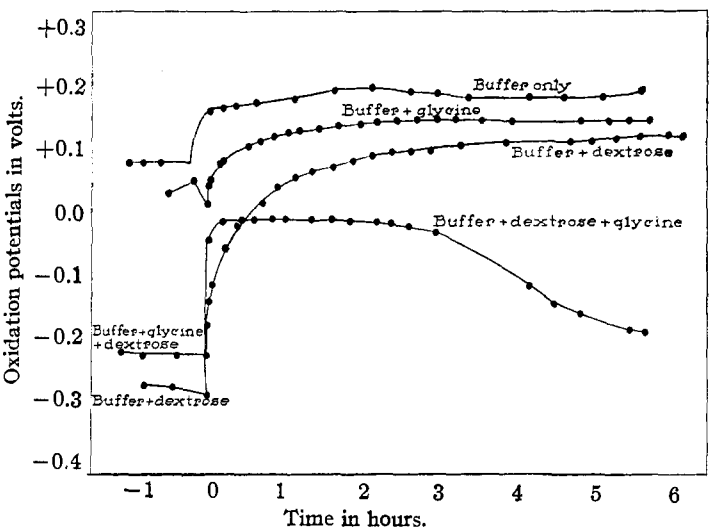

Fig. 2.—Potential drop occurs only in presence of both amino acid and dextrose; 0.5 cc. of 0.03% H_2O_2 added at time zero.

When three other amino acids were tried, glutamic acid, aspartic acid and tyrosine, there was no drop in potential within six hours after the addition of hydrogen peroxide (Fig. 3). The curves for these amino acids are essentially like those for dextrose alone.

The results described were obtained with solutions of hydrogen peroxide made up by diluting commercial 3% hydrogen peroxide solution until the titration indicated 0.03% of hydrogen peroxide by weight. This source of hydrogen peroxide with its trace of acetanilide was used because of constancy of composition. Since it was feared that the acetanilide might possibly be modifying the results, the experiment next described was tried. Glycine and glutamic acid were selected as examples of amino acids with

[4] Kendall and Nord, *J. Biol. Chem.*, **69**, 295 (1926).

and without marked catalytic action. Hydrogen peroxide, 0.03% by weight, was made by diluting a stronger solution which contained no acetanilide. This solution was added immediately after standardization as in the former experiments. It was found that the acetanilide in the concentration used had no appreciable effect on the shape of the curves (Fig. 4).

Discussion of Results

Our results are necessarily qualitative. The drifts of potentials in solutions in the absence of appreciable amounts of the components of a reversible system of oxidation-reduction are known. The values found

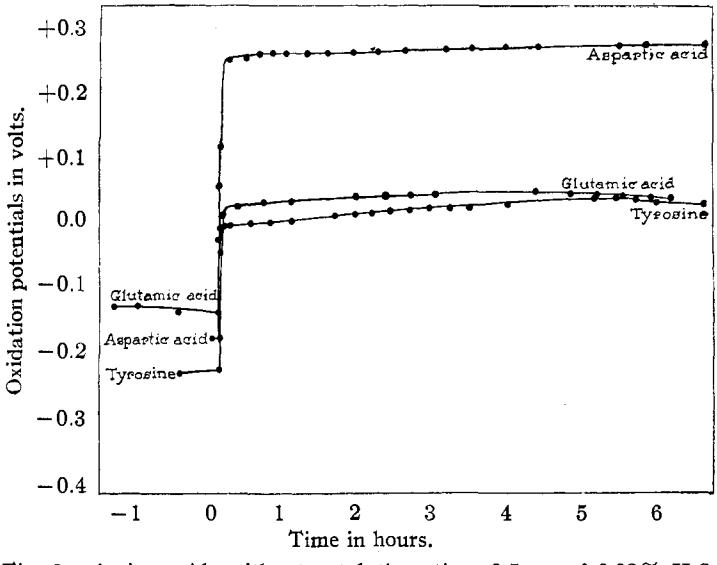

Fig. 3.—Amino acids without catalytic action; 0.5 cc. of 0.03% H_2O_2 added at time zero.

before the addition of hydrogen peroxide are especially erratic. No emphasis is placed on the exact position of the curve on the voltage scale. However, the general shape of each curve is entirely reproducible and has been duplicated many times.

The term "catalytic action" has been used in a broad sense. Undoubtedly *in vivo* and probably also in our experiments the amino acids undergo irreversible chemical decomposition. Yet certain reactions occur in their presence that do not take place in their absence, or at least only very slowly. It is known that there is some sort of reaction between certain amino acids and sugars.[5] Witzemann's quantitative work shows that glycine aids the action of hydrogen peroxide on certain fatty acids.[6]

All of our experiments were carried out on solutions in buffers containing

[5] Borsook and Wasteneys, *Biochem. J.*, **19**, 1128 (1925).

[6] Witzemann, unpublished data.

disodium phosphate. Witzemann and others have shown that phosphates alone will catalyze the oxidation of sugars.[7] Since phosphates are present in blood, it seems desirable to have them also present in any experiments which are attempted in the field of biochemical oxidation. The mechanism of such oxidation is, of course, largely unknown. The effect of the slightly higher body temperature on the catalytic action of these substances is yet to be studied. Our experiments were carried out at P_H 10.00, which is more alkaline than the blood. Glycine at P_H 7.4 exhibits a slight catalytic action but most of the amino acids do not. It may be that much of the actual oxidation *in vivo* is carried out in organs, the cells of which have a

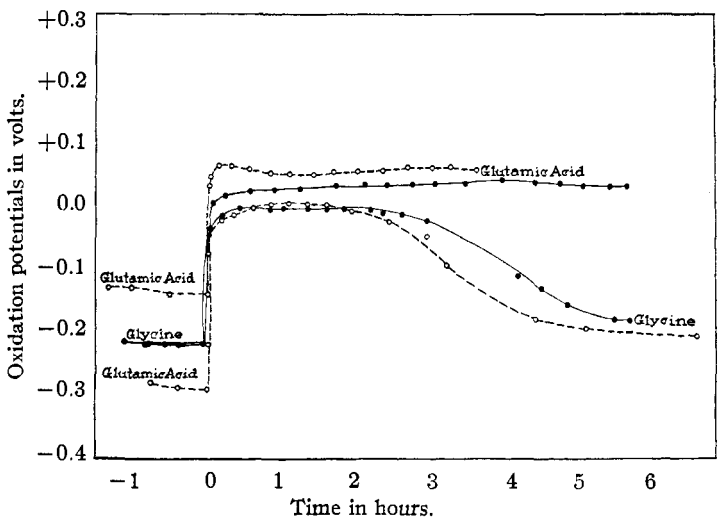

Fig. 4.—Acetanilide in traces without much effect; 0.5 cc. of 0.03% H_2O_2 added at time zero; solid line, trace of acetanilide; dotted line, no acetanilide.

P_H greater than 7.4. The structure of the membranes and the membrane potentials in these organs also probably play a large part in increasing reaction tendencies already present. Nevertheless, a striking parallelism exists between the catalytic effect of glycine, alanine, phenylalanine, leucine, glutamic acid and aspartic acid on the oxidation of dextrose by hydrogen peroxide *in vitro* and the specific dynamic action of these substances *in vivo* as reported by Lusk and others.[8]

Summary

The action of hydrogen peroxide on dextrose both in the presence and in the absence of certain amino acids was studied by the method of oxida-

[7] Witzemann, *J. Biol. Chem.*, **45**, 1 (1920).

[8] Lusk, "The Elements of the Science of Nutrition," Saunders, Philadelphia, **1919**, 3rd ed.,

tion potentials. Cystine, glycine, alanine, phenylalanine, leucine, histidine and valine were found to catalyze this action, while glutamic acid, aspartic acid and tyrosine did not affect it. This division of amino acids according to physicochemical properties closely parallels their division *in vivo* according to their specific dynamic actions.

ROCHESTER, MINNESOTA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF KITASATO INSTITUTE]

THE SYNTHESIS OF CERTAIN QUINOLINE AND ACRIDINE COMPOUNDS

BY KONOMU MATSUMURA

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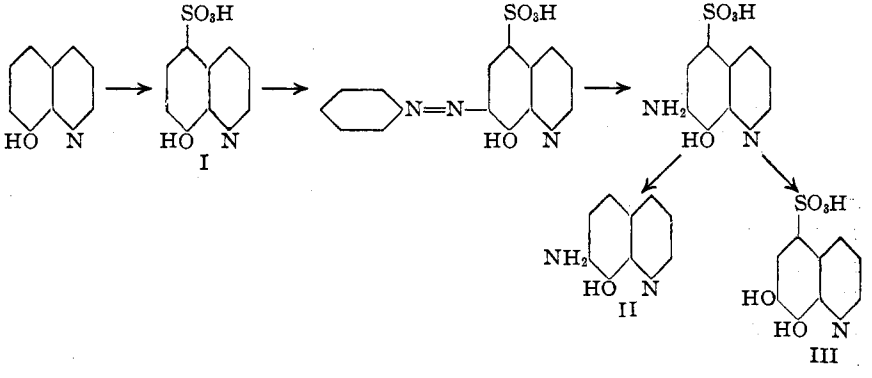
In a study of the physiological action of certain derivatives of quinoline and acridine, the author has prepared a number of compounds related to yatren (the sodium salt of 7-iodo-8-hydroxyquinoline-5-sulfonic acid) which is at present much used in medicine. This paper is a report of these preparations.

I. 7-Amino-8-hydroxyquinoline and Related Compounds

Of the amino derivatives of 8-hydroxyquinoline, the 5-amino-8-hydroxyquinoline was prepared by Kostanecki,[1] and by Fischer and Renouf.[2] The author has prepared the 7-amino-8-hydroxyquinoline using the reactions represented by the following scheme.



8-Hydroxyquinoline-5-sulfonic acid (I) was first prepared by Claus and Posselt,[3] who state that it has no definite melting point but begins to decompose at 270°. The product obtained in the present work by sulfonating 8-hydroxyquinoline by the Claus method melts at 322–323°. Al-

[1] Kostanecki, *Ber.*, **24**, 152 (1891).

[2] Fischer and Renouf, *Ber.*, **17**, 1643 (1884).

[3] Claus and Posselt, *J. prakt. Chem.*, [2] **41**, 33 (1890).