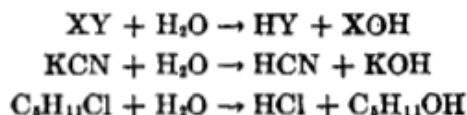


HYDROLYSIS

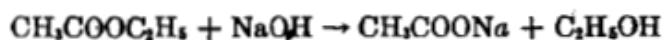
BY WILLIAM F. HAMNER AND STEWART J. LLOYD

I. DEFINITION AND SCOPE

The term *hydrolysis* is applied to reactions of both organic and inorganic chemistry wherein water effects a double decomposition with another compound, hydrogen going to one component, hydroxyl to the other:



For inorganic chemistry, hydrolysis is usually the reverse of neutralization, but in organic chemistry its scope is broader. Here it includes, among other things, the inversion of sugars, the breaking down of proteins, the saponification of fats and other esters, and the final step in the Grignard reaction, all of which can be carried on with water alone, albeit slowly and incompletely. For convenience, the meaning of the term has been extended to cover also the numerous cases in which an alkali is added to the water and in which the alkali salt of an acid is usually one of the final products:



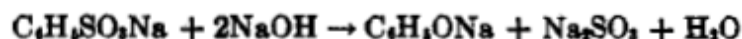
Even more common is the application of the term to reactions in which an acid is added to the water in large or small amounts. This addition, like that of alkali, invariably hastens the hydrolysis even if it does not initiate it.

Accelerating agents

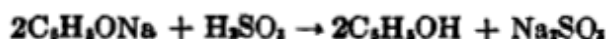
other than acid and alkali are known but, with the single exception of enzymes, are not important. The enzymes (organic catalysts) are of surpassing importance in vital processes, both animal and plant, especially in preparing food for use in the body, and many of the reactions catalyzed by them are hydrolytic.

The use of alkali in aqueous solution leads naturally to another type of hydrolytic reaction, namely, *alkali fusion*, wherein the proportion of

alkali is greatly increased and that of water correspondingly reduced, for example:



followed by



We may recognize, then, five types of hydrolysis:

1. Pure hydrolysis where water alone is used.
2. Hydrolysis with aqueous acid, dilute or concentrated.
3. Hydrolysis with aqueous alkali, dilute or concentrated.
4. Alkali fusion, with little or no water but at high temperatures.
5. Hydrolysis with enzymes as catalysts.

Acid Hydrolysis. In 1811, Kirchoff observed that starch was transformed by aqueous mineral acids into glucose and showed that no acid was used up in the process. Braconnot, in 1819, hydrolyzed linen (cellulose) with strong sulfuric acid, obtaining a fermentable sugar. This use of acid in hydrolysis was rapidly extended to other classes of organic materials—the esters, sugars, amides, etc.—and it was found that, wherever water brought about hydrolysis, acid accelerated the reaction. In addition,

Hydrochloric and sulfuric acids are naturally the most commonly used, though many others have been explored. Formic and trichloroacetic appear to be lower in activity than would be expected, whereas oxalic and benzenesulfonic are more active than sulfuric. Concentrations from very high to very low are used in both laboratory and commercial practice.

Sulfuric acid is particularly useful because it forms, with many types of organic substances, intermediate compounds that themselves readily undergo hydrolysis. This is exhibited in the acid process of fat splitting to make fatty acids, in making alcohol from ethylene, and probably also in the hydration of acetylene to make aldehyde. In all these, sulfuric acid exhibits a specific action, distinct from its hydrogen-ion concentration, and cannot be replaced by other acids.

The preparation of individual amino acids by the hydrolysis of proteins is generally very difficult because these natural materials are composed of

some 20 amino acids having similar chemical properties. Generally, no one amino acid constitutes more than 10–20 per cent of the protein. Because of this inherent difficulty, the industrial production of amino acids from casein and soybean proteins awaits further progress in current research.

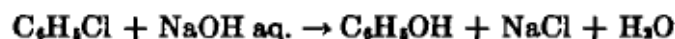
One protein that is used in multi-million-pound quantities annually is wheat gluten—which is valued for its relatively high (35–40 per cent) content of glutamic acid, $\text{HOOC}(\text{CH}_2)_2\text{CH}(\text{NH}_2)\text{COOH}$. Monosodium glutamate is a condiment that is being used in increasing quantities for imparting a meatlike flavor to soups and other foodstuffs. The usual procedure for making monosodium glutamate involves hydrolysis of the gluten with a constant-boiling 20 per cent hydrochloric acid solution; removal of excess HCl by distillation; and filtration from humin followed by successive crystallizations of glutamic acid hydrochloride, glutamic acid, and monosodium glutamate in the presence of decolorizing carbon.¹

Although acid and alkali may frequently be used interchangeably on the same materials to give essentially the same products, this is not invariably true. The action of acid on acetoacetic ester and its derivatives leads to acetone, carbonic acid, and alcohol and its related products, while alkali on the same ester produces acetic acid and alcohol.

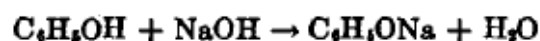
Alkali Hydrolysis. We may distinguish three different cases of hydrolysis with alkali:

1. The use of low concentrations of alkali in the hydrolysis of esters and similar materials: Here the hydroxyl ion is supposed to catalyze the reaction as the hydrogen ion does in catalysis by dilute acid. Since one of the products of reaction is usually an acid that reacts immediately with the hydroxyl ion, this case is of significance only in theoretical studies, where an instantaneous value of a reaction velocity is desired.

2. The use of sufficient caustic under pressure and in high concentrations to unite with all the acid produced:



sometimes followed by

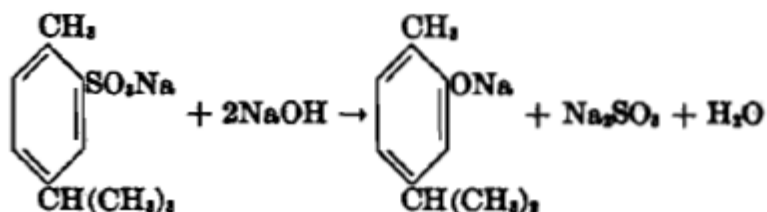


A variant of this is the passage of the vapors of chlorinated hydrocarbons mixed with steam over solid alkaline materials, such as lime, yielding alcohols.



3. The fusion of organic materials with caustic soda or potash: This develops naturally from case 2 by decreasing the ratio of water. The

formation of carvacrol from sodium *p*-cymenesulfonate is an example:



with, of course, the subsequent acidulation of the sodium salt.

This alkali fusion process is limited essentially to sulfonic acids, though the elimination of carbon dioxide is sometimes accomplished in this way.¹ Chlorinated and nitrated compounds do not seem to have been successfully subjected to this mode of treatment.

Alkali is used only to a limited extent in the hydrolysis of carbohydrates. Cellulose is rather resistant to alkali and, when attacked, is broken down but not distinctly hydrolyzed. The carbohydrates in corn cobs undergo deep-seated changes when heated at 240°C with a concentrated caustic solution, oxalic and acetic acids being the principal products. When invert sugar is treated with two molar equivalents of sodium hydroxide—as a 50 per cent solution—lactic acid is obtained.²

Caustic soda is the base most commonly used, but the alkali carbonates and bicarbonates as well as the alkaline-earth hydroxides all find occasional application. Potassium compounds show no advantage over the cheaper sodium materials, except that potassium hydroxide in some alkaline fusions permits the use of a lower temperature. Ammonium hydroxide and ammonium salts are rarely used. Chloroform has occasionally been used as a solvent.

Compression of solid catalysts like silica gel used for hydrolysis reactions has been studied in Russia, the results showing that in the particular case in question the improvement in yield passed through a maximum with increasing pressure.³

Enzymatic Hydrolysis. Comparatively few large-scale operations depend upon enzymes for hydrolysis, though one or two enzymes (urease) are used for analytical purposes. Molasses is converted by invertase in the manufacture of industrial alcohol, and, of course, the whole brewing industry depends upon the complex hydrolysis of starch into maltose and glucose by the amylases. Despite its occasional industrial application, enzymatic hydrolysis is, however, primarily the concern of the biochemist.⁴