

The Chemical Effects Produced by Ultrasonic Waves

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Abstract:- Ultrasonic treatment of a water solution causes, as is well known, some chemical effects depending on the phenomenon of cavitation. Several investigators have devoted attention to these chemical effects, being principally effects of oxidation and reduction, and have tried to explain them in various ways. In general it is assumed that dissolved oxygen in some way is activated in the course of cavitation. However, there are reasons indicating that the water molecule itself may be decomposed by ultrasonic treatment and that the effects of oxidation, though to a less extent, are noticeable even when oxygen is absent.

Keywords: Chemical effects, ionizing radiation, ultrasonic waves

INTRODUCTION

In this way the ultrasonic waves have effects similar to those of the ionizing radiation⁽¹⁾ from radioactive preparations. The chemical effects of ionizing radiation have been subject to much investigation, the application of this knowledge to the corresponding conditions associated with ultrasonics seems simple, in addition to being of considerable value⁽²⁾.

Schematically and very briefly⁽³⁾, it may be stated that certain chemical effects⁽⁴⁾ in water solutions of the ultrasonic waves-or, more correctly, of cavitation may be explained in the following way: According to our experimental results⁽⁵⁾ we assume as the primary characteristic reaction:



This reaction is regarded as the fundamental and typical reaction produced by electric discharge in water vapor and by ionizing radiation on water vapor⁽⁶⁾ and water solutions⁽⁷⁾. What then happens with the primarily produced free radicals is of a complicated and not yet fully established nature. Experiments show a production mainly of hydrogen peroxide, hydrogen, and oxygen. If now it were possible to establish the presence of free radicals in water solutions subjected to ultrasonic waves, the analogy between cavitation-chemical and radiochemical effects could be stated more conclusively.

Investigating radiochemical reactions in water solutions, Dainton has studied⁽⁸⁾ the polymerization of acrylonitrile in water solution. The polymerization was initiated by the free radicals produced by ionizing radiation from strong radioactive preparations. We therefore, thought it suitable to investigate whether the ultrasonic waves might bring about a similar effect.

RESULTS AND DISCUSSION

Experiments concerning the polymerization of acrylonitrile in water solution induced by ultrasonic treatment have given positive results. In support of the opinion that the polymerization is initiated in the way indicated, the authors desire to adduce the following:

(1) Some possible effect of dissolved oxygen is eliminated in these experiments. The solutions were degassed by boiling under a reflux condenser. In some experiments the solutions were degassed in vacuum and the ultrasonic treatment performed in an atmosphere of nitrogen. Furthermore, the ultrasonic waves themselves have a strong degassing action. Oxygen is a strong inhibitor in the polymerization of acrylonitrile. The positive result of these experiments is therefore an indication of the absence of oxygen.

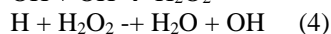
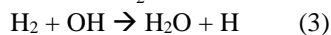
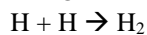
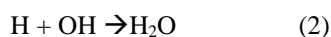
(2) The possibility of the reaction being induced by some catalyst present as an impurity is gainsaid by the fact that not even boiling for a meek could bring about polymerization or any other change of the acrylonitrile solution used in the experiments.

(3) It is conceivable that the ultrasonic waves by oxidation or in some other way destroy any inhibitor substances. Any catalysts present will then start the polymerization. If this assumption were correct the polymerization, after being initiated by the ultrasonic waves, would continue even after the ultrasonic treatment has been interrupted. This, however, is not the case.

(4) Some catalyzing effect of the material in the reaction vessel is not probable. The reaction is the same, whether the oscillating parts of the reaction vessel are made of platinum, copper, or glass. According to the hypothesis of

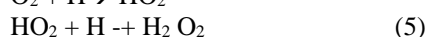
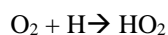
the authors some of the chemical effects of the ultrasonic waves can be explained in a simple way.

What happens with the free radicals after the primary dissociation of water evidently depends on the many, often very intricate factors that influence the chain reactions where the chain carriers are free radicals⁽⁹⁾. However, the predominant reactions are probably the back-reactions⁽¹⁰⁾:



When water free from impurities is treated with ultrasonic waves the net result will thus be zero, since the equilibrium concentrations of hydrogen peroxide and hydrogen may be too small to be detected.

The presence of dissolved substances in the water will increase the possibilities of other reaction series than the proper back-reactions. Especially compounds with a high vapor pressure, which may occur in a higher concentration in the cavities, will take part in the secondary reactions. Possible reactions in the presence of dissolved oxygen are:



Hydrogen atoms are to some extent withdrawn from the back-reactions 2, 3, and 4. Simultaneously the corresponding amount of hydroxyl radicals will react with other oxidizable substances. This is in agreement with the fact, established by several investigators in this field, that dissolved oxygen greatly increases the oxidation effects of ultrasonic waves and that the amount of hydrogen peroxide observed is too small to explain these oxidation effects. These circumstances are generally explained by stating that oxygen is directly activated by the ultrasonic waves according to the equation:



Such a reaction is obviously possible and will occur simultaneously with reaction 1. However, the concentration of oxygen is small compared with that of water, even in the cavities. We must therefore conceive of reaction 1 as the predominant reaction. For that reason the influence of dissolved oxygen in this connection is best represented by equation 5, whereas equation 6 is of secondary importance. In this way it is possible to explain most of the chemical reactions produced by ultrasonic treatment of water solutions, e.g., oxidation of potassium iodide, hydrogen sulfide, organic dyestuffs, and hydrocarbon halides such as chloroform; reduction of potassium permanganate and mercuric chloride; production of NH_3 , NH_2OH , NO_2^- , and NO_3^- ; in the presence of dissolved nitrogen.

Quantitative investigations of the matter discussed above are difficult to carry out. Reactions where free radicals are essential components are not easy to survey.

In addition, the reproducibility is not good, since extremely small amounts of impurities may have a considerable influence on the course of the reaction series. A further complication, compared with the corresponding radiochemical investigations, is the insufficient reproducibility of the cavitation as such.

THEORETICAL DETAILS

The kinetics of the ultrasound-induced polymerization of acrylonitrile in dilute aqueous solutions may be explained in the following way:

The free radicals (1) primarily produced are involved in various secondary reactions, some of which have been indicated above. At steady-state conditions a constant fraction of the primarily and secondarily produced free radicals is available to induce the polymerization of the present monomer. However, the production of these free radicals is not the only cause of the polymerization reaction. An analysis of the experimental results will show that in addition there is a kind of autocatalytic effect⁽¹¹⁾. This effect can be ascribed to the well-known depolymerizing effects of the ultrasonic waves. Thread molecules of colloidal size, subjected to strong ultrasonic vibration, suffer such strain that C-C bonds may be broken. The end-groups at the fracture may be unsaturated and of a radical nature like the active end-group in a growing polymer molecule⁽¹²⁾. The fragments obtained in the splitting of a polymer molecule are thus capable of continued polymerization.

The following abbreviations are introduced for the subsequent treatment. In the chemical equations⁽¹³⁾ they refer to chemical individuals and in the mathematical equations to concentrations of these species in moles per liter.

M = monomer, MO = initial concentration, R = radical groups of the growing polymer,

P = polymer, n = the average number of monomers in the polymer,

p = fraction polymerized, and t = time in hours.

As above, it is assumed that a constant fraction of the radicals produced in the cavitation is available for participation in the polymerization reaction.

Cavitation \rightarrow H, OH (participating in the polymerization reaction).

CONCLUSION

The experimental results will show that in addition there is a kind of autocatalytic effect. This effect can be ascribed to the well-known depolymerizing effects of the ultrasonic waves. Thread molecules of colloidal size, subjected to strong ultrasonic vibration, suffer such strain that C-C bonds may be broken. The end-groups at the fracture may be unsaturated and of a radical nature like the active end-group in a growing polymer molecule. The fragments obtained in the splitting of a polymer molecule are thus capable of continued polymerization.

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