form of calcium sulfate which has existence in the range 0-200°. "Soluble anhydrite" is identical in crystal form with hemihydrate, and the solubility curve formerly given as that of "soluble anhydrite" is the curve for hemihydrate. Hemihydrate is metastable in the approximate range 90-130°, showing decreasing stability with decrease of temperature below 90° and with increase of temperature above 130°.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

OXIDATIONS PROMOTED BY ULTRASONIC RADIATION

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During the course of an investigation of the effects of ultrasonic radiation on certain photosensitive reactions, it was found that iodine was liberated from an aqueous solution of potassium iodide by such radiation. It was subsequently discovered that other reactions were sensitive to this agency; indeed Richards and Loomis,[2] using a 2-kilowatt oscillator, have reported two cases in which they observed some stimulation.

Experimental Methods

The high-frequency mechanical vibrations were generated in a manner already described.[3] The electrical oscillations were produced by a single 250-watt tube tuned to the natural frequency of the quartz crystal, which was about 750 kilocycles per second. In the cases of almost all reactions reported in the present paper, the reactants were contained in a test-tube dipping into the liquid dielectric immediately over the crystal. In this way the energy was transmitted to the solution in the test-tube, resulting in vigorous cavitation of any dissolved gas, the escaping bubbles being momentarily caught in the nodes of the standing wave system. In certain reactions it was desirable to render the liquid free, to all practical purposes, of dissolved gases before radiation. This was accomplished by boiling for three or four minutes in a test-tube fitted with a valve. On cooling the tube the valve closed, excluding the air indefinitely. In other reactions in which the presence of only one gas was desired, the liquid was rendered air-free in the manner already described; the valve was removed and a layer of mineral oil laid over the surface; the gas to be dissolved was then bubbled in from a fine jet. The use of oil had certain disadvantages and it was never employed unless absolutely essential. In order to ascertain whether electrical oscillations were responsible for the observed effects, a test-tube containing the reactants was placed above

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[2] Richards and Loomis, THIS JOURNAL, **49**, 3086 (1927).

[3] Schmitt, Olson and Johnson, *Proc. Soc. Exptl. Biol. Med.*, **25**, 718 (1928).

the dielectric, another test-tube within the induction coil and a small receptacle containing potassium iodide and starch solution was inserted between the electrodes and the circuit tuned. In none of these experiments was any reaction observed, although the solutions within the induction coil, and between the electrodes, became hot.

Reactions Involving Gases

I. Oxidation of Halide Ions.—The oxidations of halide ions in neutral solutions by atmospheric oxygen in the dark are extremely slow reactions. If a 1 *N* aqueous solution of potassium iodide saturated with air under atmospheric pressure is subjected to ultrasonic radiation, iodine is liberated. When potassium iodide–starch reagent is added to aqueous solutions of potassium bromide and potassium chloride which have been radiated in the same way, the starch–iodine color appears immediately; if distilled water is radiated and tested in this manner no color appears until after a lapse of four or five minutes. Either the bromide and chloride ions are oxidized in these experiments or some other substance is produced in the presence of these salts which oxidizes the iodide ion instantaneously. To test the influence of positive ions 1 *N* potassium nitrate and 1 *N* potassium sulfate solutions were treated as above. Both of these solutions behaved essentially like distilled water but the rates of development of color were noticeably faster. To test further the influence of the positive ions, the above experiments were repeated with 1 *N* solutions of sodium and lithium salts and precisely similar results were obtained. Since Li^+ is considered to be highly hydrated in solution, the effect of hydration appears not to be important. It was also demonstrated that the hydrogen-ion concentration has a marked influence upon the rate and extent of color production. Although the halides showed an immediate color upon adding the starch–iodide reagent, the intensity of color developed by these solutions on standing in the dark for half an hour was as follows: $I^- > NO_3^- > SO_4^{--} > Cl^- >$ water $> Br^-$.

The depth of color produced by a three-minute period of radiation of potassium iodide solution is of the same order of magnitude as that produced by one part in a million of hydrogen perioxide. To test for the formation of hydrogen peroxide, titanium sulfate reagent was irradiated. Positive results were obtained in the majority of the trials; all of these solutions were sensitive to one part of hydrogen peroxide in three million parts of water. The formation of ozone was also suspected and it was tested for with manganous sulfate in acid solution. The tests were negative, but it is likely that this method is not sufficiently sensitive to justify the conclusion that no ozone was formed.

It is well known that the presence of ions influences the sensitivity of the starch–iodide test. Very dilute solutions of hydrogen peroxide were therefore added to starch–iodide reagent containing potassium salts. When potassium iodide was the salt added, a distinct color appeared immediately; with other salts a lapse of from one to three minutes occurred before color developed. The relative rates of color production in these experiments, under comparable conditions, were as follows: $I^- > NO_3^- > SO_4^{--} > Cl^- >$ water $> Br^-$. On standing in the dark for half an hour these solutions showed approximately the same depth of color although exhibiting some differences in shade.

The influence of the sulfate and nitrate ions in the case of the radiated solutions may merely have been upon the sensitivity of the starch–iodide test; but the immediate apppearance of color with bromide and chloride, on addition of the reagent after radiating, indicates some additional factor. This may be the production of free bromine and chlorine by oxidation of the halide ions.

2. **Oxidation of Hydrogen Sulfide.**—Aqueous solutions containing hydrogen sulfide and air, when radiated for a few minutes, become strongly opalescent due to the oxidation of the hydrogen sulfide to sulfur, the latter appearing in the form of a colloidal precipitate. An attempt was made to estimate the amount of hydrogen sulfide which was oxidized under the influence of a three-minute period of radiation, by determining the strength of a solution of sodium thiosulfate required to react with sulfuric acid and yield a solution of the same degree of opalescence as an average radiated sample. The assay indicated that three minutes' radiation caused the oxidation of about 0.2 cc. of hydrogen sulfide gas, under standard conditions, from 5-cc. samples of solution. In this case, again, the rate of oxidation of an aqueous solution of hydrogen sulfide to sulfur by air alone is a reaction which even over a period of days does not proceed to any appreciable extent. A mixture of equal volumes of a 3% solution of hydrogen peroxide and of the aqueous solution of hydrogen sulfide produced opalescence at a much slower rate than that observed under the influence of ultrasonic radiation.

3. **Oxidation of Organic Halogen Compounds.**—A very striking result was obtained when a clear aqueous solution of carbon tetrachloride was radiated in the presence of starch and potassium iodide. The blue color of the starch iodide compound developed immediately; at the end of one minute of radiation the tube was practically opaque and the color many times deeper than that obtained by three minutes' radiation of potassium iodide and starch alone. Air and water must both be present for this reaction to occur.

If a two-phase system, carbon tetrachloride and aqueous potassium bromide solution, is radiated, the aqueous phase quickly becomes yellow due to the liberation of bromine. A number of other experiments involving organic compounds are now in progress and the results will be communicated in a later paper.

4. **Reduction by Gaseous Hydrogen.**—A solution of ferric ion through which hydrogen had been passed for a sufficiently long time to remove the dissolved air was radiated for five minutes. The resulting solution was tested for ferrous ion by potassium ferricyanide, and also for a change in the ferric-ion concentration with ferrocyanide and thiocyanate. In the most carefully controlled experiments no reduction could be detected. Had the amount of reduction been comparable to the amount of oxidation found in the former experiments, these tests would have been sufficiently delicate to detect the change.

Reactions not Involving Gases

Having succeeded in inducing reactions involving oxidations by oxygen under the influence of ultrasonic radiation, it next became necessary to determine whether slow reactions which proceed in the absence of oxygen could similarly be accelerated. Two reactions have already been studied by Richards and Loomis,[2] namely, the hydrolysis of dimethyl sulfate, and the iodine "clock" reaction, and the conclusion drawn that, after controlling the reactions as carefully as possible for differences in integral temperatures, there was a residual difference in rates which indicated that the radiation produced a 10% acceleration.

In certain of our experiments along quite different lines, in which Brom Thymol Blue was used and apparently positive results were obtained, it was suspected that the indicator itself was affected rather than that the reaction had been stimulated. Subsequent tests showed that when a dilute aqueous solution of Brom Thymol Blue (to which sufficient sodium hydroxide was added to produce a blue-green color) was radiated, the solution changed to yellow in a very short time. It was easy to demonstrate that comparatively few of the dye molecules were destroyed in the process of radiation, for addition of alkali caused a prompt return of the blue color. Other indicators, such as Brom Phenol Blue and litmus were affected in a similar manner. Whatever the process may be, there is no doubt that dye molecules were altered by the radiation and gave rise to hydrogen ions.

In the experiments of Richards and Loomis on the hydrolysis of dimethyl sulfate, Brom Thymol Blue was used to indicate the course of the hydrolysis. Since, during radiation, a sufficient amount of this indicator is decomposed to affect the color of the remaining indicator molecules, it follows that their results are not yet complete enough to justify their conclusions. We have shown above that if an aqueous solution con-containing dissolved oxygen is radiated, hydrogen peroxide or something analogous to it is formed. This must contribute to the acceleration of the iodine "clock" reaction observed by Richards and Loomis. Since the solutions employed by them were acid, any hydrogen peroxide produced by the radiation would transform the iodate to iodine independently of the mechanism of the "clock" reaction.

It will be shown in a later section of this paper that considerable importance must be attached to the cavitation of a gas from the reacting solutions. Consequently, all solutions at present under consideration were kept free of gases during the course of the reaction. In order to maintain the same sensitivity of test as in the previous experiments, all the reactions chosen involved the oxidation of iodide ion. Briefly, starch-iodide solution was added to three oxidizing agents, chlorate, arsenate and nitrite ions, respectively, in acid solution. Manipulation of the ionic concentrations and of P_H values permitted suitable regulation of the rates of oxidation. After mixing, the solutions were rendered free of gases and subjected to radiation, a control tube similarly treated but not radiated being kept in each experiment. The results can be summarized as follows. The oxidation of iodide ion proceeded slowly in all cases but in none of the experiments was it possible to state definitely that an increase in the reaction rate occurred, as a result of from five to fifteen minutes of radiation. Moreover, cavitation of nitrogen from solution during the course of the reactions produced no appreciable acceleration. It is evident that if any stimulation of these reactions occurred, the amount of such stimulation was small compared to that observed when oxygen was present.

The Effect of Pressure.—It is probably significant that the reactions which have been accelerated by ultrasonic vibrations have involved at least one gas. The oxidation of hydrogen sulfide presents the most striking example of stimulation and in this case both reactants are gases under normal conditions. To ascertain whether the oxidation occurred during the process of cavitation, on the assumption that the formation of an interface is essential to the activation of the oxygen molecules, experiments were carried out with aqueous solutions of potassium iodide containing very small amounts of dissolved air. Iodine was liberated although no bubbles were seen. Moreover, bubbling oxygen in a fine stream during radiation through an aqueous solution of potassium iodide and starch, which originally was gas-free, did not give rise to color, apparently since none of the oxygen dissolved. If an aqueous solution of potassium iodide and starch is saturated with oxygen gas under four or five atmospheres of pressure and then released, no oxidation of iodide ion occurs. It seems necessary to assume that every phase of bubble formation is realized in this process, and it must be concluded, therefore, that the mere formation of bubbles in the absence of ultrasonic vibrations is unable to effect the oxidation.

On the other hand, if solutions of potassium iodide or of hydrogen sulfide containing air were radiated for the same time at a series of increasing pressures, applied from an oxygen tank, it was found that the amount of reaction as measured by the depth of color or opalescence, respectively, slowly increased up to a certain pressure; above this critical pressure there was a sudden diminution in the reaction rate. The depth of color produced by three minutes' exposure increased somewhat with pressure, so that at a pressure of thirty-five pounds per square inch the color was definitely darker than at atmospheric pressure. Under these conditions no visible cavitation occurred during radiation. At fifty-five pounds the depth of color was still maintained, but on increasing the pressure pound by pound, a series of fainter and fainter colors was produced until at sixty-five pounds per square inch no color could be detected after three minutes' radiation. The critical pressure above which no measurable reaction takes place is an arbitrary figure depending chiefly upon the amount of dissolved gas and upon the intensity of radiation. In a series of experiments with very dilute hydrogen sulfide–air solutions, it occurred at twenty-seven pounds per square inch.

The fact that the color intensity increases slightly with pressure up to a certain point is to be expected. Increased pressure, the prevention of loss of reactants by cavitation, and the consequent minimizing of disturbances in the standing wave system produced by the larger bubbles all tend to augment the amount of reaction taking place during the period of radiation. The fact that higher pressures inhibit the reaction completely is a powerful argument against the hypothesis that individual oxygen molecules in solution can be activated directly by ultrasonic energy. A possible explanation of the phenomenon is that there exists a critical bubble size below the limits of visibility which is essential for the activation of the oxygen. Application of pressure beyond a certain amount prevents the cavitation of bubbles of this size and consequently inhibits the reaction. A pressure of seventy pounds per square inch does not affect the rate of oxidation of potassium iodide by hydrogen peroxide. The effect of pressure, therefore, must be on the rate of formation of hydrogen peroxide if this be the active agent.

It may be mentioned that the rise in temperature caused by exposing a test-tube containing 10 cc. of water at room temperature to three minutes of radiation was about 5°, both under atmospheric pressure and under an applied pressure of seventy pounds per square inch. In the latter case cavitation of air was prevented, and the piling up of the water at the meniscus noticeably increased. Yet, as stressed above, oxidations did not occur under these circumstances.

Summary

A number of substances in the presence of oxygen and water have been oxidized by subjecting them to ultrasonic radiation under such conditions that gas bubbles might be formed in the liquid.

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