

Values for $L_{D_2O} - L_{H_2O}$ calculated from this equation are given in Table III. The estimated limits of error given in Table III are derived from the estimated limits of error of the vapor pressure results. Since the necessary simplifying assumptions depart further from the facts with rising

TABLE III

VALUES FOR THE DIFFERENCE OF THE LATENT HEATS OF VAPORIZATION OF HEAVY AND LIGHT WATER, $L_{D_2O} - L_{H_2O}$, CALCULATED FROM EQUATION 2

$T, ^\circ\text{C.}$	$L_{D_2O} - L_{H_2O}$, g. cal. per mole	Estimated limit of exptl. error, g. cal. per mole
40	300	± 20
60	275	± 10
80	246	± 10
100	216	± 10
120	186	± 15
140	159	± 16
160	137	± 10
180	121	± 10
200	113	± 5
220	115	± 4

temperature, the degree of trust we can place upon these latent heat differences is measured by the degree of similarity of behavior of the two forms of water.

The value for this difference reported by Lewis and Macdonald⁷ was based on assumed rectilinearity of the $\log p_2/p_1$ against $1/T$ graph between 20 and 90°, and their value agrees with ours for a temperature near 70°.

Summary

The vapor pressures of deuterium water have been compared with those of ordinary water in the range 20 to 230°. The vapor pressures are identical at about 224°.

The differences of the latent heats of vaporization are evaluated approximately from the changes of vapor pressure over the same temperature range.

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Sonic Activation in Chemical Systems: Oxidations at Audible Frequencies

BY EARL W. FLOSDORF, LESLIE A. CHAMBERS AND WM. M. MALISOFF¹

During the past few years there have appeared numerous reports of oxidations, as well as other types of chemical reactions, induced or accelerated by intense ultrasonic vibrations.²⁻⁴

Schmitt, Johnson and Olson³ observed the liberation of iodine from potassium iodide solution. They further reported that "upon the addition of radiated potassium bromide or chloride solution to starch-iodide reagent, a blue color developed which indicated either the oxidation of the bromide and chloride ions or that some other substance is produced in the presence of these salts which oxidizes the iodide ion instantaneously. Radiated distilled water produced the effect to a less marked degree." Hydrogen peroxide was found in small amount, insufficient to account for the observed rate of oxidation of halogen or of sulfide. Ozone production, if any, was in amounts too small to be detectable and consequently could not be considered as the oxidizing

agent. It was further found that dissolved oxygen gas was essential to the oxidations and it was suggested that the gas was activated in association with ultrasonic cavitation. Direct absorption of energy by the molecules in solution was believed to be inconsistent with results that were obtained under pressures sufficient to inhibit visible cavitation.

Liu and Wu⁴ confirmed the findings of Schmitt, Johnson and Olson, in the case of potassium iodide oxidation by ultrasonic radiation, with respect to the essential presence of dissolved oxygen gas and to the insufficient production of hydrogen peroxide or ozone to account for the observed effects. Liu and Wu presented experimental evidence in favor of the view that activation of oxygen gas is associated with cavitation. It is questionable, however, whether the conditions of radiation in a gel, whereby cavitation is suppressed and no oxidation is observed, are otherwise sufficiently comparable to justify without further evidence their conclusion concerning the influence of cavitation.

(1) Fellow of the Josiah Macy, Jr., Foundation. Now at the Montefiore Hospital, New York City.

(2) Richards and Loomis, *THIS JOURNAL*, **49**, 3086-3100 (1927).

(3) Schmitt, Johnson and Olson, *ibid.*, **51**, 370 (1929).

(4) Szu-Chik Liu and Hsien Wu, *ibid.*, **56**, 1005 (1934).

Beuthe⁵ also has suggested that the primary effect of ultrasonic radiation is upon the dissolved gases. He concluded, however, from his study of the ultrasonic oxidation of certain halides, that the intermediate formation of hydrogen peroxide and possibly of ozone is at least partially responsible for the liberation of the free halogen. Oyama⁶ has likewise reported the oxidation of pure water by ultrasonic action.

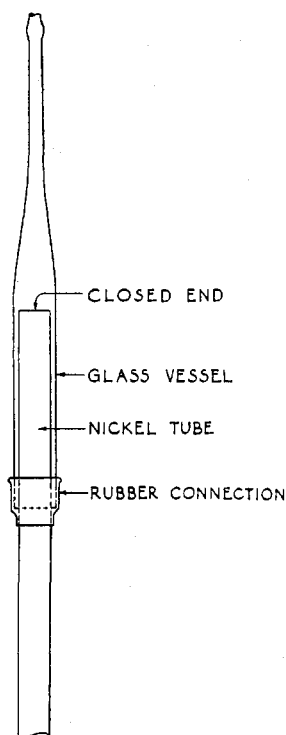


Fig. 1.—Reaction vessel, oscillator MS.

It should be emphasized that the experiments in which the above observations were made, in each case, were carried out through the use of ultrasonic vibrations (10^5 to 1.5×10^6 cycles/second). Apparatus for investigating the effects of intense sounds in the audible range (12 to 1.8×10^5 cycles/second) has been developed by Gaines⁷ and used by Chambers and Gaines⁸ and their collaborators, in various studies of the biological and physical actions of such audible vibrations. With this audible sound source we have extended the survey of the chemical effects of intense sound into the audible range (Flosdorf and Chambers⁹). Qualitatively, the effects produced

(5) H. Beuthe, *Z. physik. Chem.*, **A163**, 161-171 (1933).

(6) H. Oyama, *Radio Research Japan*, **4**, 41-55 (1935).

(7) Newton Gaines, *Physics*, **3**, 209-229 (1932).

(8) Chambers and Gaines, *J. Cell. Comp. Physiol.*, **1**, 465 (1932).

(9) Earl W. Flosdorf and L. A. Chambers, *THIS JOURNAL*, **55**, 3051 (1933); **56**, 2795 (1934).

at 9000 cycles/second seem to be similar to those previously reported for ultrasonic frequencies. Since the available sound densities are greater within the audible band the effects are greater in degree making quantitative studies less tedious and difficult and consequently more accurate.

In this paper we shall present some results of a quantitative study of certain oxidation reactions sonically activated in the audible range. We have undertaken to determine the conditions under which these sonic oxidation reactions take place in an aqueous medium, the reactants involved, the rates of reaction, and the sound intensities required. Particular attention is devoted to the question of the possible intermediate roles of hydrogen peroxide and of sonically activated oxygen. Although technical limitations have restricted the accuracy of our data, the results are instructive in a consideration of the intermediary mechanism involved not only in oxidative activation but in sonic reactions generally.

Experimental

Two types of apparatus were used, (1) the magnetostriction oscillator described by Gaines⁷ and by Chambers and Gaines⁸ (hereafter referred to as oscillator MS) and (2) an electromagnetic oscillator (oscillator EM).⁹⁻¹¹

In oscillator MS, a cold-drawn, unannealed nickel tube, 20 mm. in diameter, vibrates in a strong electromagnetic field in resonance with a 2000 volt oscillating power circuit to which the tube imparts approximately its own natural frequency. The tubes used in these experiments, 250 mm. long, produce a frequency of about 8900 cycles per second with an acoustic output of about 15 watts (estimated) under full load. A rubber connection supports a glass vessel on the metal tube (Fig. 1). In each experiment 17-20 ml. were treated. The entire quantity was required for a single test sample which necessitated a fresh start for each time interval studied.

The diaphragm of oscillator EM is 33 cm. in diameter. The oscillator produces a frequency of about 1200 cycles per second with a maximum output of about 175 watts (Submarine Signal Co. estimate) under full load. It is of a type used in under-water signalling and depth-finding and is manufactured by the Submarine Signal Company of Boston. An iron cylinder 20 cm. deep is bolted to the periphery of the stainless steel diaphragm forming the bottom of the treatment vessel. Up to four liters of solution can be treated at one time and test samples can be removed at intervals from the same initial solution leaving sufficient for further treatment.

It has not been possible to eliminate all rubber and metal parts from contact with the reacting mixtures in either oscillator without serious impairment of intensity. Until

(10) Earl W. Flosdorf and L. A. Chambers, *J. Immunol.*, **28**, 297-310 (1935).

(11) L. A. Chambers and Earl W. Flosdorf, *J. Biol. Chem.*, **114**, 75-83 (1936).

this is accomplished the extent of catalytic action of traces of foreign substances cannot be ascertained.

It has been found that none of the sonic oxidations previously reported⁹ occur in water boiled free of oxygen and accordingly all the experiments in this study, unless otherwise stated, have been carried out with free access of air to the liquid. With the energy intensities we used, cavitation is suppressed with hydrostatic pressures over six atmospheres. Since we have found the oxidations to progress only with sonic cavitation, the experiments were carried out in the presence of air at atmospheric pressure. All the results included in this report were obtained with the solutions at a temperature of 20 to 30°.

The analytical results were obtained by the following methods. *Hydrogen peroxide* was titrated in sulfuric acid solution with 0.002 *M* potassium permanganate. Results were accurate to within $\pm 20\%$. *Sodium bisulfite* was determined by titration with potassium permanganate to an estimated accuracy of $\pm 5\%$. *Free chlorine* (or hypochlorite) was determined colorimetrically with *o*-tolidine in hydrochloric acid solution.¹² The readings were made seven minutes after addition of the test reagent. These determinations were accurate to within $\pm 10\%$. *Chlorate* was qualitatively detected after removal of chloride and hypochlorite by reduction with sodium nitrite and subsequent precipitation with silver nitrate.

Quantitative Results

(1) **Hydrogen Peroxide Formation.**—With either oscillator hydrogen peroxide has been found to be produced from water and oxygen in quantities that are of the same order of magnitude as those reported for ultrasonic frequencies.^{3,4} These quantities approach 300 micro-equivalents per liter in periods under an hour; the amounts are measurably increased by vibration in acid solution such as in 0.01 *M* sodium bisulfate. Under the latter condition the reaction is interfered with, however, by the sonically accelerated side reaction of the metal of the vibrator with the acid.⁹

The rate at which the production of hydrogen peroxide takes place in pure water is illustrated in Fig. 2. Under the conditions of these experiments the estimated power output of oscillator EM was approximately ten times that of MS, whereas for EM there was twenty times the volume of water to vibrate. The amounts of chemical change per unit of energy *output* from the two sources of sound therefore appear to be about the same, in spite of the frequency difference. The spray produced as a result of the vigorous cavitation apparently is sufficient to keep the solution adequately saturated with oxygen inasmuch as the concentration of hydrogen peroxide does not reach

a constant value up to the maximum duration of treatment studied. Furthermore, a stream of air bubbling through the solution during treatment produced no detectable increase in the rate.

Iodine liberation, titrated by sodium thiosulfate as used by Liu and Wu,⁴ did not yield any indication of measurable production of ozone. Hydrogen peroxide, determined by permanganate titration, was produced in sufficient quantity within the limits of experimental error to account for all the iodine liberated.

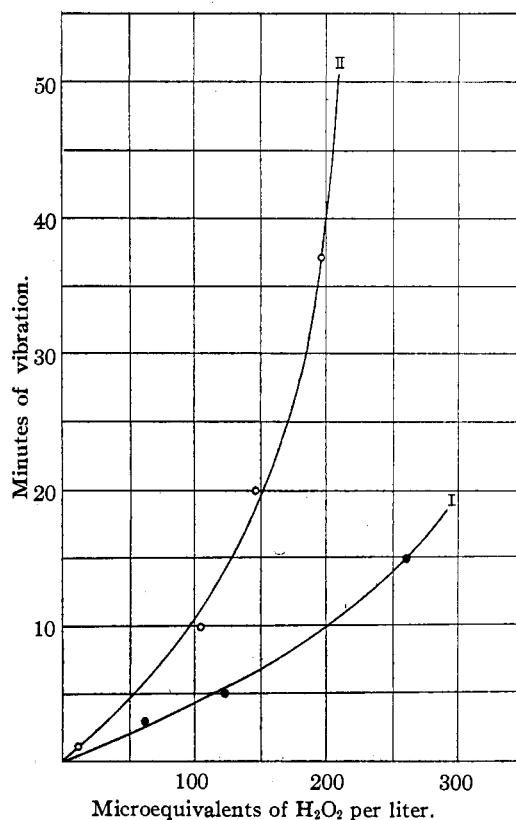


Fig. 2.—Treatment of pure water; Curve I, oscillator MS; Curve II, oscillator EM.

In alkaline solution, 0.002 *M* potassium permanganate is rapidly reduced to manganese dioxide as is to be expected on the basis of hydrogen peroxide formation. Reduction reactions of hydrogen peroxide do not lend themselves to quantitative study in the oscillators, however, because of the complicating factor introduced by the accelerated reduction reactions of the metal of the vibrators.⁹ Oxidation reactions involving direct addition of oxygen therefore would seem to be simpler for study. Furthermore, in order to avoid any possible sonic action directly on a test reagent itself, analytical reagents in general

(12) J. W. Ellms and S. J. Hauser, *J. Ind. Eng. Chem.*, **5**, 915, 1030 (1913).

should not be added to test samples until after they are removed from sonic apparatus. We shall now proceed to the results obtained from oxidation reactions involving the addition of oxygen.

(2) **Sodium Bisulfite Oxidation.**—Sodium bisulfite oxidation has not been studied in the ultrasonic range. We have found it to be oxidized relatively rapidly in the audible range in either oscillator, the rate being dependent upon the molarity of the bisulfite. A typical result obtained in oscillator EM is illustrated in Fig. 3. In

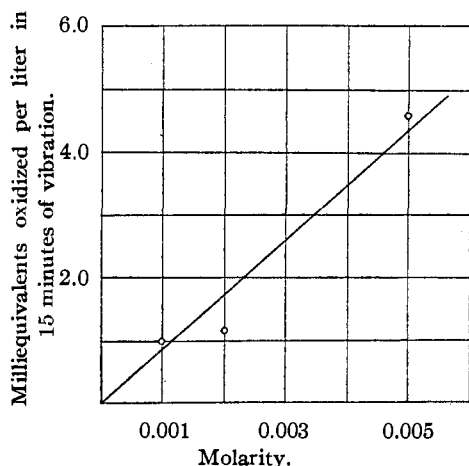


Fig. 3.—Oxidation of sodium bisulfite in oscillator EM.

Table I it will be noted that with 0.04 molar bisulfite as much as 19.2 milli-equivalents per liter have been oxidized in sixty minutes which is about seventy times as fast as hydrogen peroxide has been shown to accumulate. Upon completion of the oxidation of the sodium bisulfite we have found hydrogen peroxide is produced at about the same rate as in sodium bisulfate solution.

TABLE I
TREATMENT OF SODIUM BISULFITE SOLUTION, OSCILLATOR MS

Molarity (approx.)	Duration, min.	Milli-equivalents oxidized per liter
0.0007	5	0.2
	15	.5
	60	1.4
.04	10	13.1
	60	19.2

Contrasted with the production of hydrogen peroxide in the two oscillators where the amounts of chemical change per unit of energy are approximately equal, the oxidation of bisulfite proceeds only about one-fifth as fast in oscillator MS as in EM. In oscillator EM there is much more vigor-

ous spraying into the air. Because of the more rapid rate of the bisulfite reaction, this condition which controls the dissolution of oxygen to maintain the supply of gas in solution may be critical. Otherwise, we must assume that the difference in frequency is a factor in the oxidation of bisulfite and not of water.

(3) **Oxidation of Chlorides.**—In order to avail ourselves of the advantages of a system not sensitive to light, chloride was the halogen ion chosen for quantitative study. The rate of chlorine production (the test samples are acidified with the hydrochloric acid of the test reagent which completely liberates the chlorine from hypochlorite)⁹ has been found to be dependent upon the concentration of chloride, Fig. 4, but not in as

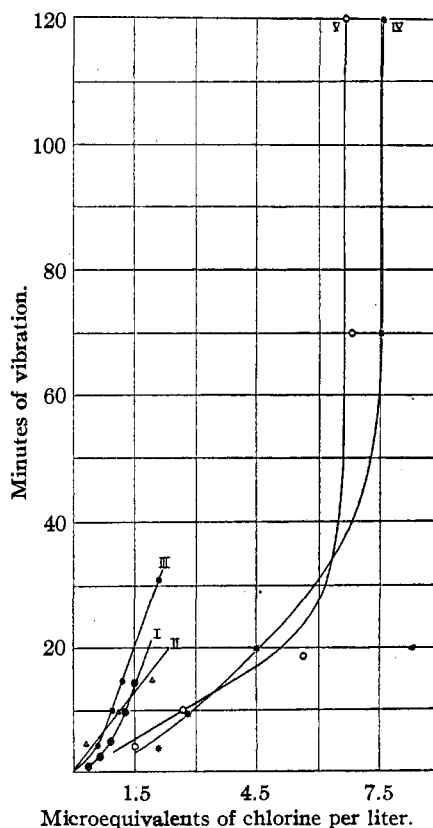


Fig. 4.—Oxidation of sodium chloride.

Chlorine determinations made after ten minutes of standing following vibration.

Oscillator MS, curve I, 0.5 Molar
Oscillator MS, curve II, 2.0 Molar
Oscillator EM, curve III, 0.5 Molar
Oscillator EM, curve IV, 2.0 Molar
Oscillator EM, curve V, 5.0 Molar

great degree as the bisulfite reaction. The amounts of chlorine found in solution increase with duration of treatment but reach a limiting concentration of the order of 7 to 8 microequiva-

lents per liter. This is probably a result of the loss of chlorine gas from solution. In solutions of high pH , oxidation of chloride is very slow. In neutral solution the pH increases slightly during treatment because of hypochlorite formation.⁹

The quantity of chlorine found in solution is in part dependent upon the length of time of standing before the test reagents are added, subsequent to treatment. With quantities produced under 0.3 micro-equivalent per liter, the amount is doubled after standing for ten minutes. With larger quantities the amount may be increased by as much as one micro-equivalent. This suggests that accumulated hydrogen peroxide may be responsible for at least the continued effect subsequent to removal of the solutions from the oscillators. In Fig. 5 the quantities of chlorine produced by known amounts of hydrogen peroxide and sodium chloride are given. Up to 100 micro-equivalents of hydrogen peroxide per liter would be required to produce the additional chlorine found in ten minutes of standing, which is consistent with the known rate of production of peroxide. That the rate of reaction of hydrogen peroxide with chloride is slow is evident from the fact that with 2 M sodium chloride and 1200 micro-equivalents of peroxide per liter, the amount of chlorine produced in ten minutes is 3.7 micro-equivalents per liter and in twenty minutes is 4.5. The effect of the concentration of chloride and of peroxide is shown in Table II.

TABLE II
EFFECT OF DILUTE HYDROGEN PEROXIDE SOLUTION ON
SODIUM CHLORIDE

Concentration after mixing Hydrogen peroxide, micro-equivalents per liter	Sodium chloride, molarity	Time of standing be- fore testing, min.	Chlorine produced, micro-equivalents per liter
6000	0	10	0.0
6000	2	10	6.5
1200	2	10	3.7
1200	1	20	2.5
1200	2	20	4.5
1200	5	20	7.9

It is further apparent, however, that the known rate of production of peroxide cannot account for all the chlorine formed. In ten minutes in oscillator EM, three micro-equivalents of chlorine per liter are produced from 2 M sodium chloride, which, on the basis of Fig. 5, would require 700 micro-equivalents of peroxide per liter for the intermediate step mechanism. We have never found in either oscillator more than 200 micro-equivalents of peroxide in ten minutes. Likewise,

with oscillator EM, in thirty minutes 6000 micro-equivalents of peroxide per liter would be required to yield the observed amount of chlorine, yet there never were indications of more than 300. Furthermore, peroxide is produced at a higher rate per liter in oscillator MS and we should expect, accordingly, a greater production of chlorine in this oscillator were the intermediate peroxide step essential for the production of all the observed chlorine; but more chlorine is found in oscillator EM.

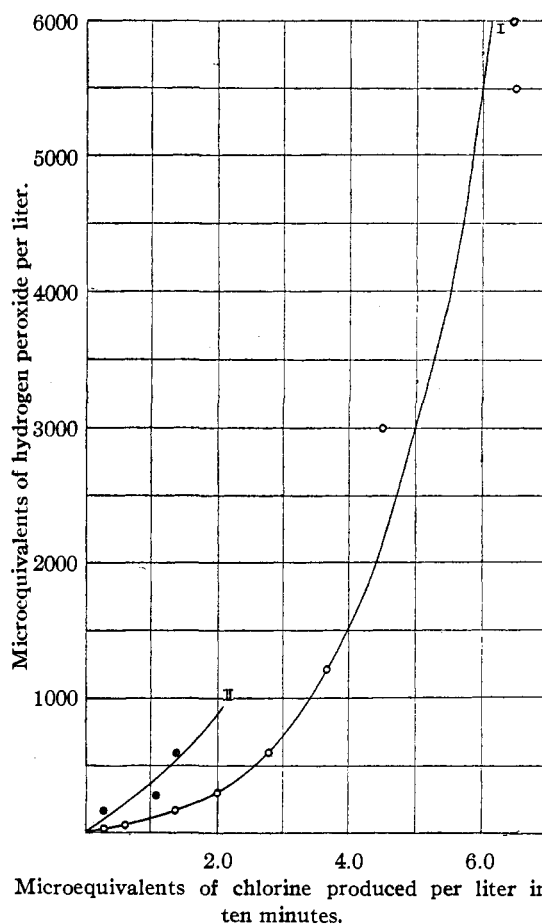


Fig. 5.—Reaction of dilute hydrogen peroxide solution with sodium chloride: curve I, 2 M sodium chloride; curve II, 1 M sodium chloride.

That sonically produced very dilute hydrogen peroxide solution can cause the production of chlorine is further evident from the data in Table III.

Water was treated by sound, removed from the apparatus after varying durations of treatment, and added to sodium chloride solution. As much as two micro-equivalents of chlorine per liter were produced. Sufficiently large samples can be ob-

TABLE III
EFFECT OF ADDITION OF SOUND CAVITATED WATER TO SODIUM CHLORIDE SOLUTION

Oscillator	Volume treated, ml.	Duration of treatment, min.	Concn. of H ₂ O ₂ micro-equiv. per liter		Concn. of NaCl after mixing, <i>M</i>	Time of standing before testing, min.	Chlorine produced, micro-equiv. per liter
			Produced	After mixing			
MS	17	10	Insufficient sample		2	8	1.1
	20	60	Insufficient sample		2	20	2.0
EM	500	1	12	7	2	10	0.0
	450	10	106	65	2	10	0.6
	400	20	147	88	2	10	1.0
	350	37	194	124	2	10	1.1

tained from oscillator EM to permit the determination of hydrogen peroxide as well as of chlorine and, within the limits of experimental error, the quantities of both which have been found agree with the values to be expected on the basis of Table II. It is again evident, however, that the hydrogen peroxide is produced in insufficient quantity to account for all the chloride that was found to be oxidized sonically.

The possibility has not been ruled out, however, that under the influence of sound, the reaction of sonically produced hydrogen peroxide with chloride is accelerated sufficiently to account for the twenty-fold increase in the rate of production of chlorine that takes place in the oscillators. On the basis of this mechanism, however, it is difficult to account for the more rapid production of chlorine in oscillator EM which takes place in spite of a lower rate of formation of peroxide. It would be difficult to understand how there could be a difference in degree of acceleration of peroxide reaction in the two oscillators because of the frequencies when there is apparently little or no frequency effect on the production of the peroxide.

The possibility that chloride-ion catalytically increases the production of peroxide to such an extent that the latter would oxidize chloride-ion at the observed rate does not seem to be tenable. This mechanism also would involve a frequency effect.

To us it seems rather that the twenty-fold increase in rate of chlorine production, and particularly the seventy-fold increase in rate of bisulfite oxidation, suggest the possibility of a chain reaction similar to that in the thermal and in the photochemical bisulfite reactions.¹³ If so, this suggests the activation of oxygen and the chains should be breakable by the usual alcohol inhibitors. These possibilities are to be investigated further.

(13) H. N. Alyea and H. L. J. Bäckström, *THIS JOURNAL*, **51**, 90 (1929).

It would seem, therefore, that there are two concurrent reactions taking place in which chloride is oxidized, *viz.*, the direct oxidation with activated oxygen and secondary oxidation with sonically produced hydrogen peroxide. On this basis the curves in Fig. 4 would represent the total effect of the two reactions. The net result would seem to be that maintenance of an adequate supply of oxygen in solution becomes the critical factor which explains the difference in rates in the two oscillators, or else there is a frequency difference responsible for more rapid oxidation of chloride in oscillator EM. More probably it is a question of oxygen supply. The sonic spray is so effective in exposing solution surface to the air for dissolution of oxygen, however, that bubbling air through the solution produces no detectable effect.

(4) **Chlorate Production.**—After standing overnight, test samples of sonically cavitated chloride solutions continue to show the presence of one to two micro-equivalents of chlorine per liter, provided they have been stored in the presence of hydrochloric acid of the concentration used in the *o*-tolidine test. Solutions of chloride to which sonically cavitated water or hydrogen peroxide solution (up to 1000 micro-equivalents per liter) has been added do not continue to show chlorine after standing overnight, the gas having been completely lost. The gas remaining in solution the next day has been attributed to the slow production of chlorine from the hydrochloric acid and sonically produced chlorate. This has been confirmed qualitatively by the detection of minute amounts of chlorate in sonically treated chloride solution by reduction with sodium nitrite after removal of chloride and hypochlorite and subsequent precipitation of the reduced chlorate with silver nitrate.

(5) **Oxidation of Organic Compounds of Chlorine.**—We have determined also that organic chlorine compounds, such as chloroform and

carbon tetrachloride, are oxidized as a result of sonic cavitation. Free chlorine and chloride ion are produced. Schmitt, Johnson and Olson³ and Liu and Wu⁴ have reported that a similar effect is obtained by ultrasonic vibration.

Sonic Chemiluminescence

The reaction by which light is produced as a result of the oxidation of "luminol" (3-aminophthalhydrazide) we have found to be interesting because it affords a visual confirmation of the importance of cavitation in sonic oxidation. We have determined that this reaction can be carried out sonically with dissolved oxygen gas as the only source of oxidant.

Harris and Parker¹⁴ have shown that in the luminol reaction with hydrogen peroxide and another oxidant "the light-emitting molecule is a compound of sodium luminol and hydrogen peroxide, or this compound is the parent of the light-emitting molecule. The light-emitting molecule is brought to its energized state by reactions of the parent with some oxidizing molecule." We have found that as little as 50 micro-equivalents of hydrogen peroxide per liter is sufficient concentration to make the reaction visible in the dark without dark adaptation upon the part of the observer. It seemed reasonable, therefore, to expect luminescence by the sonic reaction in which the sound would be the sole energy source of hydrogen peroxide and oxidant. Two-tenths gram of luminol was dissolved in 20 ml. of 5% sodium hydroxide and 0.1 ml. of this stock solution in 10 ml. of distilled water was used for sonic vibration.

Upon vibration of such a solution either in oscillator MS or EM luminescence is easily visible. After allowing the observer's eyes to become dark-adapted for ten minutes the distribution of the light production becomes distinguishable. In addition to the bright glow to be seen at the top of the nickel tube (oscillator MS) streamers of light are observed to rise in spirals from the tube just as the cavitation vacuoles rise. Throughout the solution, points of light may be noticed and if these points of maximum intensity be marked and the electric lights switched on, it is seen that the spirals and the points of maximum light intensity correspond exactly with the positions of maximum cavitation. The light of greatest intensity apparently is produced in association with cavitation vacuoles.

(14) Louis Harris and A. S. Parker, *THIS JOURNAL*, **57**, 1930 (1935).

The maximum luminescence is produced immediately or is made to vanish immediately with the turning on or off of the oscillator. After more prolonged and continuous vibration (five to ten minutes), however, a faint and homogeneous afterglow persists for five or ten minutes after the vibration ceases and it appears throughout the entire solution.

With the use of the vacuum vessel previously described in connection with the investigation of egg albumin,¹¹ luminescence is observed as described above. If after such vibration in which luminescence is produced, the solution in this vessel is boiled under vacuum (60 mm.) and thoroughly swept with nitrogen and finally left under one atmosphere of nitrogen, no luminescence can be observed upon subsequent sonic vibration although cavitation occurs as usual. If then this same solution is saturated once more with oxygen by bubbling air through it, luminescence is again visible as before upon sonic vibration.

It seems definitely established, therefore, that hydrogen peroxide is produced from dissolved oxygen and water upon sonic vibration and that this reacts with sodium luminol to form the light-emitting molecule or its parent substance. This parent is then brought to its energized state by reaction with some oxidizing substance. The much greater intensity of luminescence which occurs at the cavitation surface than that found existing as a faint afterglow throughout the body of the solution after more prolonged vibration (the latter presumably being entirely due to accumulated hydrogen peroxide) indicates that the oxidizing substance which brings the parent molecule to its energized state is being produced in these regions. The substance may be either activated oxygen or newly formed hydrogen peroxide in high concentrations in thin layers, as yet unmixed, or both. By analogy with the oxidation of chloride, we could expect reaction of the parent substance with both activated oxygen and with hydrogen peroxide. This greater intensity of luminescence at the cavitation surfaces by reaction with activated oxygen is analogous to that produced by potassium ferricyanide (without sonic vibration), in which case the parent substance is produced with as little as 50 micro-equivalents of hydrogen peroxide per liter.

Discussion

It is obvious from theoretical considerations

that the activation of dissolved oxygen may not be attributed to sound waves *per se* in the fluid. Furthermore, the experimentally established fact that such activation occurs only during sonic cavitation of the liquid and only in the immediate vicinity of such disruptive disturbances, indicates that we must be dealing with a phenomenon not easily amenable to theoretical treatment. From the evidence at hand we may conclude that oxygen is brought into a reactive state during some phase of cavitation through a process not understood at present. The activated oxygen is then free to react with either solute or solvent molecules. A similar conclusion was drawn by Schmitt, Johnson and Olson,³ and by Liu and Wu⁴ from experimental data relative to oxidations promoted by ultrasonic cavitation.

That oxygen is not the only gas capable of activation during cavitation of its solvent has been demonstrated in previous papers. For example it already has been shown^{10,11} that egg albumin is denatured by sonic cavitation in the presence of carbon dioxide as well as oxygen, while in the presence of nitrogen or hydrogen, or in gas free solution, no denaturation occurs even during vigorous cavitation.

One may assume perhaps that molecules of the high energy necessary to permit the formation of hydrogen peroxide from molecular oxygen and water are created during sonic cavitation through a process of ionization or excitation. While no theoretical justification for such an hypothesis can be drawn from acoustical theory it should be remembered that, in the events accompanying cavitation, we are not dealing with acoustical phenomena *per se*. As a matter of fact the recent observation by Chambers¹⁵ that visible light is emitted from pure polar liquids during cavitation by sound waves of the same amplitude as those

(15) L. A. Chambers, *Bull. Am. Phys. Soc.*, **11**, No. 2, 30 (1936) (Abst. 114).

used in our experiments lends credibility to the supposition that excitation or ionization may actually be occurring.

Whatever the mechanism it would appear from the evidence in hand that activation of oxygen during cavitation offers the best explanation for the chemical changes recorded in our experiments. With improvements in apparatus it should be possible to obtain further data which will permit calculation of the reaction orders and to carry out experiments of greater theoretical significance. Some means of estimating quantitatively the relative degrees of sonic cavitation produced in liquids and means for experimental variation of this factor will ultimately be necessary.

Acknowledgment.—We wish to express our appreciation to Mr. David Lackman for the assistance he has given in the chlorine determinations.

Summary

Quantitative studies of the oxidation of water and of sodium bisulfite and sodium chloride in aqueous solution by cavitation produced at audible frequencies have been carried out. The data indicate that the oxidations are accomplished through the production of activated oxygen in association with cavitation. It was determined that a compound of sodium luminol and sonically produced peroxide may be energized to produce chemiluminescence in the absence of the usual secondary oxidants, the reaction giving visual confirmation that chemical activation occurs during sonic cavitation. The results represent an elaboration of earlier work in the audible range and an extension to the audible of effects previously observed in the ultrasonic range. Some effects new at either range have been reported and certain theoretical conclusions have been drawn which probably are general for all frequencies.

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