855. *The Chemical Action of Ultrasonic Waves.*

By A. V. M. PARKE and DUNCAN TAYLOR.

Spectra of the sonoluminescence from aerated bromine water and from aerated aqueous carbon disulphide solution have been examined with a resolution not better than 100 Å. In each case, a broad band in the visible region was detected. For water containing argon, air, oxygen, or nitrogen the intensity of sonoluminescence as measured by a photomultiplier increased with time of irradiation up to equilibrium values which varied linearly with ultrasonic power. Oxidation due to ultrasonic waves increased linearly with time of irradiation in the solutions O_2–H_2O, O_2–KI–H_2O, air–KI–CCl_4–H_2O, A–H_2O, N_2–H_2O, while for the first three the rate of oxidation increased linearly with both ultrasonic power and the intensity of sonoluminescence. For oxygen–water solutions, addition of salts (except potassium iodide) and of sulphuric acid had no effect on the luminescence or oxidation, but for O_2–KI–H_2O solutions a three-fold increase in the rate of liberation of iodine occurred without change in luminescence when the pH was reduced from about 7 to 2. Nuclear hydroxylation of aromatic molecules when irradiated in aqueous solution was observed. The results are discussed in the light of current theories for the action of ultrasonic waves.

NUMEROUS investigations [1-6] of the oxidising action of ultrasonic waves on aqueous solutions have led to the following general conclusions: (*a*) simultaneous occurrence of cavitation and sonoluminescence is essential; (*b*) the action, while more pronounced in presence of dissolved oxygen, also occurs if the dissolved gas is argon, nitrogen, or carbon monoxide; for potassium iodide solutions oxidation is greatly increased by dissolved carbon tetrachloride; (*c*) hydrogen, carbon dioxide, and volatile organic substances such as ether and acetone, but not carbon tetrachloride or carbon disulphide, inhibit the effects. Miller [3] has drawn

[1] Prudhomme and Grabar, *J. Chim. phys.*, 1949, **46**, 318, 323, 667.
[2] Weissler, Cooper, and Snyder, *J. Amer. Chem. Soc.*, 1950, **72**, 1769.
[3] Miller, *Trans. Faraday Soc.*, 1950, **46**, 546; *J. Chim. phys.*, 1951, **48**, 242.
[4] Lindström, *J. Acoust. Soc. Amer.*, 1955, **27**, 654.
[5] Griffing, *J. Chem. Phys.*, 1950, **18**, 997; 1952, **20**, 939.
[6] Griffing and Sette, *ibid.*, 1955, **23**, 503.

attention to the analogy between the chemical effect of ultrasonic waves and that of ionising radiation, and he and other workers [1, 7] have suggested that the oxidising action is "indirect" and consistent with a primary process $H_2O \longrightarrow H + OH$ occurring in the cavities. No direct evidence for the existence of hydroxyl radicals, similar to that of Weiss and his co-workers [8] for ionising radiation, has yet been reported. To account for the primary process, the most widely accepted theory is that of Frenkel,[7] who considers that lens-shaped cavities are oppositely charged on the two faces owing to a non-equilibrium distribution of ions, a subsequent discharge across the cavities being responsible for both the breakdown of water molecules and the sonoluminescence. Prudhomme and Grabar [1] have added that the breakdown may be photochemical provided the luminescence contains a component of sufficiently short wavelength. On the other hand, Noltingk and Neppiras [9] (cf. Griffing [5]) have calculated that during the adiabatic collapse of cavities temperatures of the order of 10,000° may be realised momentarily, thus suggesting thermal dissociation of water and incandescence of gas molecules in the cavities. Marboe's "mechano-chemical" theory [10] involves the breaking of O–H bonds (as distinct from hydrogen bonds) when the liquid water is torn apart during cavitation, and compares sonoluminescence with the ultraviolet luminescence observed by Audubert [11] during the neutralisation of acids and bases.

The following work on the luminescence and chemical effects and their interrelations was undertaken mainly to shed further light on the primary process.

EXPERIMENTAL AND RESULTS

Ultrasonic Generator.—This was the Mullard instrument, type E7562, with interchangeable quartz crystals 4·5 cm. in diameter giving frequencies of 0·5, 1, and 2 Mc./sec. A relative measure of the intensity of the ultrasonic beam for a given set of experimental conditions is given by the square of the voltage applied to the crystal. At 0·5 Mc./sec., calorimetric experiments showed a linear relation between the square of the voltage and the heating effect (and thus the intensity) of the ultrasonic beam, and that the range of acoustic power available in the majority of the experiments was 1·2—4·1 w cm.$^{-2}$.

Hydroxylation of Benzoic Acid and Other Aromatic Compounds.—The irradiation vessel (referred to below as vessel I) was a glass tube 6 cm. in diameter, flanged at the lower end and sealed to the face of the transducer head carrying the quartz crystal *via* a thin rubber gasket and brass clamp. The crystal was thus in contact with the solution to be irradiated. Excessive temperature rise was prevented with a glass cooling coil and air was bubbled slowly through the solution during the two-hour irradiation period at maximum power at 0·5 Mc./sec. Saturated benzoic acid solution (50 ml.) was irradiated, concentrated to small volume and filtered, and spots of the filtrate were run on paper chromatograms with a mobile phase of ethanol–water–concentrated ammonia solution (20 : 4 : 1 v/v). The three monohydroxybenzoic acids were chromatographed for comparison, the *ortho*-acid being detected by fluorescence and the *meta*- and *para*-acids by spraying with a solution of *p*-nitrophenylhydrazine which has been treated with nitrous acid as in diazotisation, and exposing to ammonia to give orange spots. The results conclusively showed that all three monohydroxy-acids were formed. A rough estimate of the relative proportions of the three isomers was made by chromatographing spots of the irradiated solution under the same conditions on two separate paper strips. One strip was treated to show the position of the acids, the appropriate areas being cut from the other strip and the acids washed from the paper with water. To each solution were added 2 ml. of a 0·1% solution of 2 : 6-dichloroquinone chloroimide, 0·5 ml. of concentrated ammonia solution, and water to 50 ml., and the resultant coloured solutions were compared in a spectrophotometer with similarly treated known solutions of the three acids. The proportions found were $o > p > m$, and are consistent with a radical substitution process. Good evidence of hydroxylation was also obtained with saturated aqueous solutions of toluene, nitrobenzene, and phenol, but not with benzene.

---

[7] Frenkel, *Acta Physicochim. U.R.S.S.*, 1940, **12**, 317.
[8] Loebl, Stein, and Weiss, *J.*, 1949, 3241, 3245, 3256.
[9] Noltingk and Neppiras, *Proc. Phys. Soc.*, 1950, **63**, *B*. 674.
[10] Marboe, *Chem. Eng. News*, 1949, **27**, 2198.
[11] Audubert, *Trans. Faraday Soc.*, 1939, **35**, 197.

Spectrum of Sonoluminescence.—To the dark-adapted eye, sonoluminescence from air-saturated water appears as a faint bluish glow, the intensity of which is increased about six times by addition of bromine or carbon disulphide. Measurements were possible only with the last two solutions. These were contained in a 3 cm.-diameter tube, which was closed with a platinum foil base sealed on with Araldite. The tube was mounted vertically in vessel I, the outer vessel being filled with water to just above the level of the platinum. Luminescence from the solution in the smaller tube passed through a quartz window to the slit of a small Hilger quartz spectrograph. The spectrum was scanned with an E.M.I. eleven-stage photomultiplier, for which full circuit details have been given by Parke.[12] In order to secure a reasonable output from the multiplier, the slits both on the spectrograph and in front of the photocathode of the multiplier were such that the resolution was not better than 100 Å. The useful wavelength range of the multiplier was 3250—6000 Å, maximum sensitivity being at about 4000 Å.

Luminescence from saturated carbon disulphide solution showed a band from about 3700 Å up to the limit of the multiplier's range. The solution itself did not absorb at wavelengths greater than about 3500 Å. Saturated bromine water gave a similar band but the short-wavelength end terminated at about 5200 Å owing to absorption by the solution. The absence of an ultraviolet component was further suggested by the fact that the total luminescence from air-saturated distilled water measured with a photomultiplier sensitive down to 2200 Å showed no change on the addition of sodium salicylate, a solution of which fluoresces when excited by wavelengths in the range 950—3400 Å.[13]

Equipment for Sonoluminescence-intensity and Oxidation-rate Measurements.—Relative luminescence intensities were determined with a nine-stage Mazda photomultiplier and a valve-voltmeter (the multipliers and circuit details[12] were made available by Mr. S. Rodda, Edison-Swan Co. Ltd.). Experiment showed that the response of the instrument was linear with light intensity over the range of intensities encountered.

The transducer head was mounted horizontally in a glass-windowed water thermostat at 20°. In some early experiments on aerated solutions vessel I without the cooling coil was used. Later vessels were constructed either from 42 mm. diameter tubing (vessel II) or from a B40 cone joint (vessel III) and closed at the lower end with a thin glass plate sealed on with Araldite. The plate also served as a flange for clamping the vessel rigidly a few cm. above the crystal. Both the distance from the crystal to the vessel base and the thickness of the base are critical for maximum transmission of ultrasonic energy[2] and were selected by trial, the criterion being maximum luminescence from water in the vessel at a given ultrasonic power. A pump drove a stream of water between the crystal and vessel base to prevent accumulation of air bubbles, which would interfere with the passage of the ultrasonic beam by reflection at the air–water interfaces. The upper end of vessel II was closed with a rubber stopper, carrying gas inlet and outlet tubes and a third tube for withdrawing samples of the irradiated solution. Vessel III was closed with a B40 socket joint fitted with gas inlet and outlet tubes, a third tube dipping to the bottom of the vessel which allowed samples of irradiated solution to be pumped out by gas pressure, and a spoon device let in through a B19 joint so that solid in the spoon could be tipped into the solution at any time without otherwise disturbing the irradiation conditions. Distilled water, redistilled from alkaline potassium permanganate solution and stored in a Pyrex flask, was twice boiled out under vacuum and saturated with the desired gas. The water was pumped by gas pressure to the irradiation vessel, which had been swept out previously by the saturating gas, and admitted through the gas inlet tube. A suitable arrangement of two-way taps between the gas supply, water reservoir, and irradiation vessel allowed either gas or water as required to pass to the vessel. During irradiation, gas was slowly bubbled through or blown over the surface of the solution, both procedures giving very similar results in the measurement of luminescence and of oxidation rate. Cylinder oxygen and " spot " nitrogen ($<$10 p.p.m. O_2) were used after being passed through liquid-oxygen traps. To remove 0·2% of nitrogen from cylinder argon, the gas was passed over titanium sponge contained in a 26″ Mullite tube at 900°, followed by liquid-oxygen traps. The pH of the gas-saturated water was not less than 6·7. All pH values were measured with a Pye glass-electrode meter. In all experiments the photomultiplier was mounted outside the thermostat, with the photocathode about 12 cm. from the irradiation vessel and screened from any luminescence occurring in the thermostat water.

Sonoluminescence Intensity Measurements.—(a) *Dependence on ultrasonic power.* When the generator was first turned on at a given power, gas was expelled from solution by the ultrasonic waves and at the same time the luminescence increased several-fold to an equilibrium value

---

[12] Parke, Thesis, Edinburgh, 1955.

[13] Miller and Brown, *Trans. Faraday Soc.*, 1955, **51**, 1623.

(with uncontrollable random fluctuations of ±10%) after 1—3 min. depending on the power and the nature of the dissolved gas. These equilibrium values were regarded as characteristic of the power applied, and were found to increase linearly with power in all cases. Relative intensities at maximum power and 0·5 Mc./sec. were 1, 1, 2·2, and 8·4 for oxygen, nitrogen, air, and argon respectively, and 12 for both bromine water and carbon disulphide solution when they were left exposed to the atmosphere during irradiation with no gas bubbling through the solution. The results also suggested a power threshold below which no luminescence occurred.

(b) *Dependence on temperature.* For air-saturated water in vessel I, the luminescence at maximum power and frequencies of 0·5 and 1 Mc./sec. decreased linearly with rise in temperature over the range 5—50°. In any experiment to determine luminescence or oxidation effects the passage of the ultrasonic beam inevitably caused a rise of not more than 3°. The fall in luminescence so caused could not be greater, however, than the 10% fluctuation in the measurement.

(c) *Dependence on concentration of dissolved oxygen.* Vessel II was used except that a 25 ml. pipette fitted with taps at each end of the bulb was inserted in place of the sampling tube. With maximum power at 0·5 Mc./sec. oxygen-saturated water was irradiated with no gas flowing until the luminescence rose to a predetermined value, after which the generator was switched off and the water immediately sampled by applying very gentle suction to the pipette. The oxygen concentration was measured by Winkler's method,[14] the iodine liberated being determined by absorption at 3530 Å. The small amount of hydrogen peroxide produced during irradiation, which also liberated iodine, was corrected for by being determined in a second sample of water by Ovenston and Rees's method.[15] As the oxygen concentration decreased from 100% to about 45% of the saturation value the luminescence rose approximately six-fold, the effect requiring 2—3 min. irradiation. Longer irradiation caused a small further rise in luminescence with very little change in the oxygen concentration. This further rise did not occur if oxygen was passed through or over the water during irradiation; instead the equilibrium luminescence value mentioned above was established.

(d) *Dependence on* pH *and the presence of dissolved salts.* The equilibrium luminescence value for an oxygen–water solution at 0·5 Mc./sec. in vessel II having first been determined, sulphuric acid to reduce the pH of the water to about 2 or a salt (KCl, KNO_3, K_2SO_4, KH_2PO_4) to give a 0·2M-solution was added through the sampling tube. On re-irradiation at the same power, no significant change in the luminescence was observed in any case.

Irradiation of Oxygen–Water Solutions.—In vessel II, 120 ml. of oxygen-saturated water were irradiated at a given power at 0·5 Mc./sec. for six successive periods of 2—4 min. each, a 2 ml. sample being withdrawn after each period and the hydrogen peroxide determined by Ovenston and Rees's method.[15] Experiment showed that the small change in volume due to the removal of samples had no significant effect on the rate of peroxide formation. Typical results for four different powers are shown in Fig. 1. The slow initial rates of peroxide formation are undoubtedly connected with the expulsion of oxygen from the water, subsequent establishment of equilibrium luminescence leading to higher and constant rates. A linear relation between the constant rates and relative power is suggested by Fig. 2.

The relation between equilibrium luminescence and rate of peroxide formation was determined by using solutions which had been pre-irradiated at a suitable power until a predetermined luminescence had been established. The quantity of peroxide produced during the pre-irradiation was subtracted from that found in the successive samples, thus eliminating the effect of the early slow rate. The concentration of peroxide was then found to increase linearly with time (Fig. 3). The rate–luminescence graph (Fig. 2) shows a slight curvature, but in view of the errors in the measurement of luminescence intensity (±10%) and in the calculation of rates (±5%), the apparent departure from linearity may not be significant. Fig. 2 also indicates a low-power threshold below which no peroxide is formed and the absence of peroxide at zero luminescence.

To determine the effect of salts and of sulphuric acid on the rate of peroxide formation at a given luminescence, a " split-run " procedure was adopted. After the desired luminescence was established, irradiation was continued for 3 successive periods of 2, 2, and 4 min. each respectively; the salt (0·2M-KCl, -KNO_3, -K_2SO_4, -KH_2PO_4) or acid (to give pH about 2) was then added through the sampling tube and the irradiation continued for 2 periods of 4 min. each. In no case did the addition of salt or acid cause any significant change in the gradient of the linear peroxide concentration–time graphs.

---

[14] Winkler, *Ber.*, 1888, **21**, 2843; Bairstow, Francis, and Wyatt, *Analyst*, 1947, **72**, 340.

[15] Ovenston and Rees, *Analyst*, 1950, **75**, 204.

During the above experiments, reproducibility was better when irradiation was controlled with reference to equilibrium luminescence rather than power. The former control was adopted therefore in a number of the experiments reported below.

Irradiation of Nitrogen–Water Solutions.—In vessel III and with a frequency of 0·5 Mc./sec., 70 ml. of nitrogen-saturated water were irradiated at maximum luminescence for 5 successive periods of 10 min. each. After each period, 5 ml. were withdrawn for nitrite-ion determination by Rider and Mellon's method,[16] and 5 ml. of fresh nitrogen-saturated water added to restore the original volume. Due allowance was made in the analysis figures for the successive dilutions. While the concentration of nitrite ion was found to increase linearly with time of irradiation, the rate (about 10^{-6} moles $l.^{-1}$ $min.^{-1}$) varied considerably from one experiment to another. At the end of the runs the nitrate ion concentration, obtained by Woodward's method[17] with a probable error of ±10%, was approximately half that of the nitrite. The ratio nitrate : nitrite did not change significantly on allowing the solution to stand for periods up to 1 hr. after irradiation either in the air or under nitrogen. If before irradiation the pH of

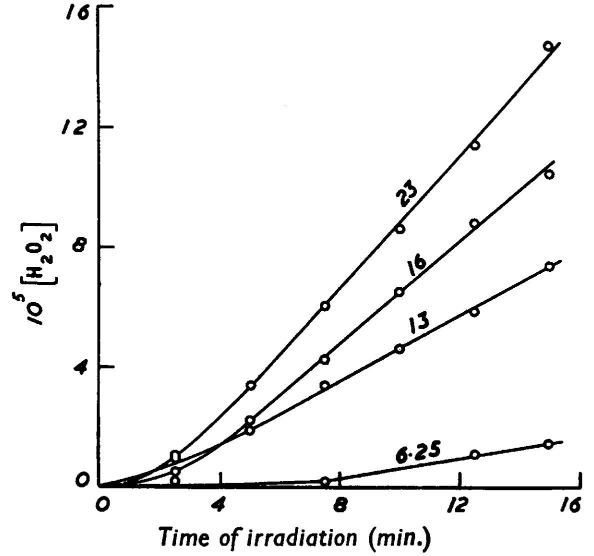

FIG. 1. *Formation of* H_2O_2 *at constant ultrasonic power in* O_2–H_2O *solutions. The numerals on the curves represent relative power.*

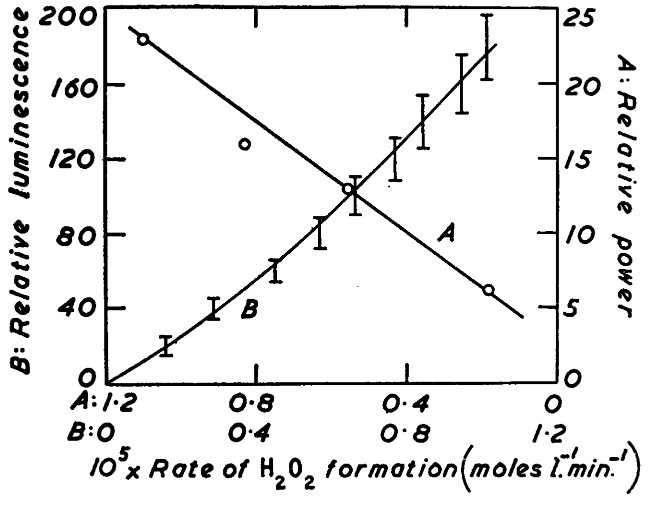

FIG. 2. *Rate of* H_2O_2 *formation in* O_2–H_2O *solutions as a function of ultrasonic power* (*A*) *and sonoluminescence* (*B*).

---

[16] Rider and Mellon, *Ind. Eng. Chem. Anal.*, 1946, **18**, 96.

[17] Woodward, *Analyst*, 1953, **78**, 727.

the water was raised to 8 or 10 by addition of sodium hydroxide, no significant change was observed in the nitrate or nitrite ion concentrations at the end of the run compared with those observed in neutral solutions; at pH 2 the ratio nitrate : nitrite in the irradiated liquid rose to 5, but the sum of the concentrations of the two ions remained unchanged.

Since Ovenston and Rees's method [15] for hydrogen peroxide was unsatisfactory in presence of nitrite ion an estimate of the peroxide formed in neutral solutions was obtained as follows.

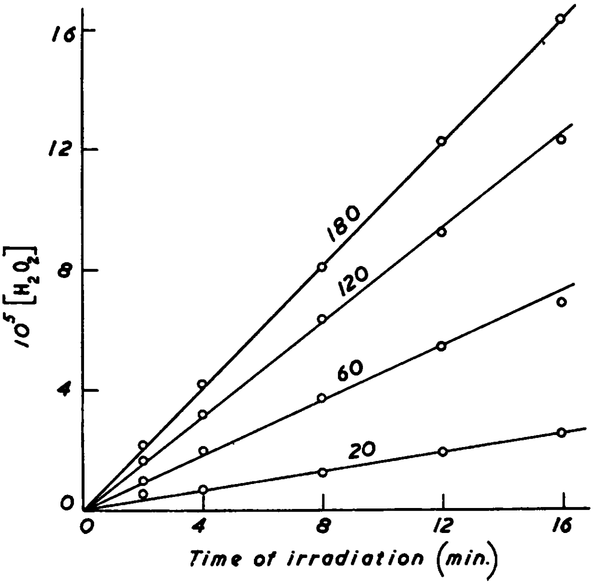

FIG. 3. *Formation of* H_2O_2 *at constant sonoluminescence in* O_2–H_2O *solutions. The numerals on the lines represent relative luminescence intensity.*

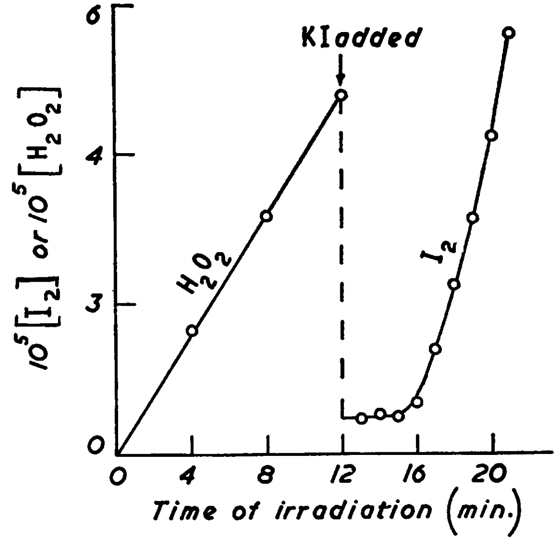

FIG. 4. *Irradiation of* KI–H_2O_2–H_2O *solutions.*

After determination of the nitrite, an equal volume of 2N-sulphuric acid and a known excess of sodium nitrite were added to a fresh portion of the solution, which was kept for 1 hr. before the residual nitrite was determined. Under such conditions, experiments with known mixtures of sodium nitrite and hydrogen peroxide showed that about 90% of the peroxide reacted, reproducibility being not better than ±20%. Within these limits, the peroxide and nitrite concentrations were found to be the same at the end of the runs. (The more satisfactory method of Schwarz and Allen [18] was published after this work was completed.)

[18] Schwarz and Allen, *J. Amer. Chem. Soc.*, 1955, **77**, 1324.

The presence of ammonium ions at the end of the runs was confirmed by Nessler's reagent, the concentration being about the same as that of nitrite or peroxide. Tests for hydrazine were negative.

In the same vessel with the same luminescence, but with irradiation periods of 2·5 min., experiments with oxygen–water solutions showed the rate of hydrogen peroxide formation to be more reproducible and 10—15 times faster than that of nitrite ion, and 3—4 times faster than that of the total products, in the nitrogen–water case.

Irradiation of Argon–Water Solutions.—With a frequency of 0·5 Mc./sec. at approximately maximum power, argon-saturated water (70 ml.) was irradiated under constant luminescence conditions in vessel III for 5 successive periods of 2·5 min. each, a 2 ml. sample being withdrawn after each period for peroxide determination. A comparative experiment with oxygen-saturated water was carried out under the same conditions. For argon solutions, the concentration of peroxide increased linearly with time at a rate about 20% less than that for oxygen solutions, although the luminescence was some eight times greater. Within the limits of experimental error, reduction of the luminescence of the argon solutions by half reduced the rate of peroxide formation in the same proportion. Argon which had not been purified with titanium at 900° gave the same results, and no nitrite or nitrate ion could be detected in solution after irradiation with full power for 25 min.

Irradiation of Aqueous Potassium Iodide–Carbon Tetrachloride Solutions in Air.—250 ml. of an aerated saturated solution of carbon tetrachloride in water containing 2 g. of potassium iodide, dissolved immediately before use, was irradiated at a given power and a frequency of 1 or 2 Mc./sec. for 1 min. in vessel I. The luminescence fell during irradiation owing to absorption by the liberated iodine, but an arbitrary value (estimated to be not more than 20% low) was taken 15 sec. after the start of the irradiation. Similar irradiations with 100 ml. of aerated solution containing 1 g. of potassium iodide were carried out at 0·5 Mc./sec. in vessel II which was left open to the atmosphere. The iodine liberated was determined by titration with sodium thiosulphate solution. It was observed that small amounts of iodine continued to be liberated slowly for about 2 hr. after the irradiation, and that results reproducible within ±5% were obtained only when the final end-points in the titrations were determined after this period. Experiment showed that the concentration of potassium iodide used was three times greater than the threshold concentration below which the liberation of iodine becomes dependent on the potassium iodide concentration. At all three frequencies the rate of iodine formation increased linearly both with power and with luminescence. The rate with full power at 0·5 Mc./sec. was about 70 times greater than that of hydrogen peroxide formation in oxygen–water solutions.

Irradiation of Potassium Iodide–Water–Oxygen Solutions.—Solid potassium iodide sufficient to give a 0·1M-solution was added to vessel II, the latter was swept out with oxygen, and then 120 ml. oxygen-saturated water were transferred to it. The solution was irradiated with a constant power at 0·5 Mc./sec. for six successive periods of 1 min. each. A 2 ml. sample was withdrawn after each period and the iodine determined by absorption at 3530 Å. The luminescence increased gradually during the first three periods and reached a constant value during the last three. As the rate of iodine liberation was many times less than that in presence of carbon tetrachloride, no significant fall in luminescence was observed. At all power values, the rate of oxidation ultimately reached a steady value (cf. Fig. 1) which increased linearly with both power and the intensity of luminescence. Under comparable conditions, the rate of iodine liberation was about 1·3 times faster than the formation of hydrogen peroxide in oxygen–water solutions, although the intensity of the luminescence was similar in both cases.

To determine the effect of pH on the rate of iodine liberation the split-run procedure described above was adopted, sufficient sulphuric acid being added to reduce the pH to between 1·35 and 2·90. Changes in the extent of the absorption at 3530 Å due to the alterations in pH were allowed for in the analyses. In all cases change of pH increased the oxidation rate by a factor of nearly three without causing any significant change in the luminescence.

If after irradiation the samples were allowed to stand, no further increase in the iodine concentration occurred. On the other hand, when oxygen-saturated water was irradiated at full power for 5 min. and then mixed with an equal volume of 0·2M-potassium iodide, the hydrogen peroxide formed during irradiation required 2 hr. to react completely with the potassium iodide, a first-order kinetic law being observed. The liberation of iodine by irradiation evidently does not proceed *via* the intermediate formation of hydrogen peroxide. The possibility remains that the normal peroxide–iodide reaction may be catalysed in some way by the ultrasonic beam. To examine this, oxygen-saturated water was irradiated at constant luminescence for three successive periods of 4 min. each, the peroxide formed being determined after each period. Solid potassium iodide was then added to make the solution 0·1M, and the irradiation continued at the same luminescence for nine successive periods of 1 min. each, the iodine liberated being measured after each minute. Typical results are shown in Fig. 4. In that part of the experiment after the addition of potassium iodide no increase in the iodine concentration of the successive samples occurred if the samples were allowed to stand for 30 min., or if the ammonium molybdate catalyst of Ovenston and Rees's method [15] was added and the sample kept for 5 min. Under irradiation, therefore, virtually all the hydrogen peroxide originally formed was destroyed, but with the liberation of only a very small amount of iodine, in 1—2 min. after the addition of potassium iodide.

DISCUSSION

Primary Process and Sonoluminescence.—The hydroxylation of aromatic molecules observed during irradiation in aqueous solution provides evidence for the formation of hydroxyl radicals and supports a primary process $H_2O \longrightarrow H + OH$. Failure to detect an ultraviolet component in the luminescence suggests that the breakdown of water molecules is not photochemical, and that sonoluminescence is not the same as the luminescence observed by Audubert.[11] Since there are no permitted electronic transitions in the water molecule that could give rise to the observed luminescence in the visible region,[13] and since the intensity was found to vary with the nature and concentration of the gas present, it seems that the light must come from excited molecules other than water. According to Frenkel's theory,[7] the intensity of the electric discharge across the cavities, and therefore the luminescence, would be expected to vary with the concentration of ions in solution. Approximate calculations have shown that addition of salts or sulphuric acid in the amounts used should have increased the cavity potentials by a factor of at least ten, yet no significant change in luminescence intensity was observed. On the other hand, increase in luminescence with increase in power and variation of luminescence with the nature and concentration of the dissolved gas are qualitatively in agreement with the theory. Furthermore, the relative luminescence order argon solutions > air solutions > nitrogen solutions is the same as the order of the first Townsend ionisation coefficients [20] for the three gases, if the coefficients are estimated by assuming potentials of the order given by Frenkel.[7] However, for hydrogen where luminescence is zero, the coefficient estimated from data given by Rose *et al.*[21] is greater than that for air.

Frenkel [7] and others have suggested an analogy between the electric potential across the ultrasonic cavities and Thomson's " ballo-electric " potential [22] on the surface of newly formed water droplets. The low value of the potential when the drops are formed in an atmosphere of hydrogen is compared with the absence of luminescence and oxidative effects in solutions irradiated in presence of hydrogen. However, Thomson also reported a fall in potential when the water from which the drops were formed in air contained sulphuric acid or potassium iodide, both of which have been shown not to reduce the luminescence or oxidation effects. In view of this, the analogy does not appear to be satisfactory.

According to the theory of Noltingk and Neppiras [9] the temperatures due to the adiabatic collapse of cavities depend upon the ratio of the specific heats of the gases present in the cavities. Luminescence being assumed to increase with temperature, the predicted luminescence order would be $A > O_2 = N_2 > Br_2 > CS_2$ whereas the observed order was $Br_2 = CS_2 > A > O_2 = N_2$. Their theory, however, does not require the luminescence to vary with the concentration of ions in solution, and in other respects appears to be not less satisfactory than Frenkel's theory. The suggested cavity temperatures of about 10,000° correspond to an energy of only about 1 ev, but a Boltzmann distribution of energies being assumed, a small fraction of the water molecules would possess sufficient energy for dissociation.

---

[19] Dewhurst, *Trans. Faraday Soc.*, 1953, **49**, 1174.

[20] Loeb, " Fundamental Processes of Electrical Discharges in Gases," Wiley and Sons Inc., New York, 1947, p. 342.

[21] Rose, De Bitetto, and Fisher, *Nature*, 1956, **177**, 945.

[22] Thomson, *Phil. Mag.*, 1894, **37**, 341.

Griffing and Sette [6] have reported non-linear relations between luminescence and power for aqueous solutions of carbon tetrachloride containing argon or carbon monoxide and for undistilled water containing air. The departures from linearity are most marked at powers greater than those used in the present work, and it is doubtful if their luminescence values are strictly comparable with the equilibrium values discussed above.

Chemical Effects.—Water with dissolved oxygen, argon, and nitrogen. Granted a primary process $H_2O \longrightarrow H + OH$ increasing linearly with power and with luminescence in any given solution, the observed linearities in the oxidation results are understandable. However, since the overall chemical activity in solution at the same power is in the order $O_2 > A > N_2$, in spite of the much higher luminescence with argon, and since oxidation and reduction of nitrogen occur, other reactions, in addition to $H_2O \longrightarrow H + OH$ with the subsequent formation of hydrogen peroxide and the very small amounts of hydrogen and oxygen reported by Prudhomme and Grabar,[1] must occur. The higher activity in presence of oxygen could be due to the reaction $H + O_2 \longrightarrow HO_2$, which would be absent with argon and nitrogen, and possibly to the activation of oxygen molecules in or on the ultrasonic cavities (cf. Bresler [23]). Activation of gas molecules is also suggested by the high luminescence in argon solutions without a correspondingly high yield of hydrogen peroxide. The formation, in nitrogen-containing solutions, of nitrite, nitrate, and ammonium ions, in addition to hydrogen peroxide, suggests interaction between H and OH and normal or excited nitrogen molecules. Increase in the ion ratio nitrate : nitrite without change in the total yield of these ions as the pH is reduced is considered to be due to the oxidising action of the hydrogen peroxide in acid solution (cf. Virtanen and Ellfolk [24]).

Potassium iodide solutions. The much higher rate of iodine liberation without notable change in luminescence when potassium iodide solutions are irradiated in presence of carbon tetrachloride, and the fact that the latter is destroyed during irradiation,[2, 6] suggest either that recombination of H and OH is reduced by their reaction with carbon tetrachloride to produce chlorine, or that carbon tetrachloride is dissociated during cavitation. The small amount of iodine liberated after the end of the irradiation could be due to reaction of iodide ions either with oxidation products of carbon tetrachloride or with traces of nitrite.

In the absence of carbon tetrachloride the three-fold increase in the rate of iodine liberation on reducing the pH from about 7 to 2 may be due to the equilibrium reaction [25] $HO_2 \rightleftharpoons H^+ + O_2^-$. On this basis, however, pH would be expected to affect the rate of peroxide formation in oxygen–water solutions, but this was not observed. The slow liberation of iodine by very low concentrations of hydrogen peroxide, in contrast to its immediate liberation by irradiation, and the absence of any post-irradiation reaction, show that hydrogen peroxide is not an intermediate in the ultrasonic reaction in 0·1M-solution. This view is supported by the surprisingly rapid destruction of peroxide with the liberation of much less than an equivalent amount of iodine when the former in low concentration was irradiated in presence of the iodide. Since other salts and sulphuric acid had no effect on the rate of peroxide formation in oxygen–water solutions, the destruction evidently involves the iodide ion. Some of Lindström's results [4] suggest a similar destruction of peroxide, and he considered that iodine in equivalent quantity was in fact formed but subsequently lost from solution by the de-gassing action of the ultrasonic waves. Loss of iodine in this way was never observed in the present work. Lindström has also reported the formation of both iodine and hydrogen peroxide when 0·0004M-potassium iodide was irradiated at pH 4. This, however, could well be due to the concentration 0·0004M being less than the threshold concentration,[2] below which the rate of oxidation becomes dependent on the iodide concentration : some of the hydroxyl radicals or activated oxygen molecules could then interact to give peroxide before encountering iodide ions.

Grateful acknowledgments are due to Dr. N. Miller for valuable discussions.

CHEMISTRY DEPARTMENT, UNIVERSITY OF EDINBURGH. [*Received, July* 13*th*, 1956.]

---

[23] Bresler, *Acta Physicochim. U.R.S.S.*, 1940, **12**, 323.
[24] Virtanen and Ellfolk, *Acta Chem. Scand.*, 1950, **4**, 93.
[25] Donaldson and Miller, *Trans. Faraday Soc.*, 1956, **52**, 652.