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The Effect of the Application of Sonic Energy to the Hydrolysis of Potassium Persulfate*

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Numerous reports of the chemical effects of audible and inaudible sound energy have been published within the last dozen years. Early experimenters in this field confined their attention to qualitative observations of the influence of sound vibrations upon diverse chemical reactions. Many of these observations concerned oxidation processes in aqueous solutions, in which the presence of dissolved oxygen has been found to be essential. The observed formation of hydrogen peroxide, by the interaction of dissolved oxygen and water, has been found to be insufficient to account quantitatively for the amount of oxidation produced: an observation leading to the conclusion that halides, sulfides, etc., may be oxidized directly by dissolved oxygen activated by sonic or ultrasonic energy.

Quantitative studies of the formation of hydrogen peroxide and of the oxidation of such inorganic compounds as sodium bisulfite and sodium chloride by sonic activation of oxygen during cavitation in aqueous solution were reported by Flosdorf, Chambers and Malisoff.[1] In the apparatus employed by these authors, a magnetostriction oscillator, as first described by Gaines,[2] was used; also an electromagnetic oscillator of the submarine signal type. The former oscillator, with a vibrating nickel tube as the source of sonic energy, was of such construction that contact with metallic nickel and rubber could not be avoided, and no provision was described for the maintenance of constant temperature of the solution being studied; the results being reported at a temperature of "20 to 30°."

It appeared to us very desirable, in view of these facts, to attempt to remove any possibility of catalytic action by metallic nickel thrown off by the vibrating element into the solution, and also to eliminate, if possible, all thermal effects to which the observed experimental results might be ascribed.

The reaction chosen for this purpose was the hydrolysis of potassium persulfate, which in the absence of added acid proceeds irreversibly according to the equation

$$S_2O_8^{=} + H_2O \longrightarrow 2HSO_4^{-} + \frac{1}{2}O_2$$

An hydrolysis was selected for this study because it was thought that, since the vibrational energy introduced into the solution was taken up so largely by the water, a reaction in which water enters as a reactant would be most suitable. Furthermore, the rate constant, k, for this reaction has been determined at several temperatures by a number of investigators, in particular, by Kailan and co-workers,[3] Green and Masson[4] and by Levi and Migliorina[5]; and these data could be used to corroborate the values obtained without the application of sound in the present work. Flosdorf and Chambers[6] also have reported that qualitatively the hydrolysis of organic substances is accelerated by the application of audible sound.

Apparatus.—The apparatus of Gaines was modified in several important respects, as described in part in a previous paper[7] on the quantitative estimation of cavitation erosion in metals. Briefly, these changes consisted of the following:

(1) The nickel tube, A (see Fig. 1), was inverted so that its closed, lower end dipped several millimeters under the surface of the liquid being vibrated. The tube was driven by magnetostrictive action at its natural vibration frequency—approximately 8700 cycles per second, determined stroboscopically—by an oscillating current tuned to the proper frequency.

(2) The driving coil, D, and feed-back coil, E, were constructed of asbestos-covered copper wire ("Deltabeston") and could be used indefinitely without failure due to overheating of the insulation, such as occurred with cotton-covered wire. The dimensions and characteristics of the two coils were as follows: Driving coil: 98 mm. O. D., 25.4 mm. I. D., 38.1 mm. thick; No. 18 wire, 24.7 m. h. impedance at 1000 cycles, 3.3 ohms D. C. resistance. Feed-back coil: 89 mm. O. D., 25.4 mm. I. D., 28.6 mm. thick; No. 22 wire, 37.5 m. h. impedance at 1000 cycles, 8.28 ohms D. C. resistance. Throughout the work the

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[1] Flosdorf, Chambers and Malisoff, THIS JOURNAL, **58**, 1069 (1936).

[2] Gaines, *Physics*, **3** 209 (1932).

[3] Kailan and Olbrich, *Monatsh.*, **47**, 449 (1926); Kailan and Leisek, *ibid.*, **50**, 403 (1928).

[4] Green and Masson, *J. Chem. Soc.*, **97**, 2083 (1910).

[5] Levi and Migliorina, *Gazz. chim. ital.*, **36**, 11, 599 (1907).

[6] Flosdorf and Chambers, THIS JOURNAL, **55**, 3051 (1933).

[7] Schumb, Peters and Milligan, *Metals and Alloys*, **8**, 126 (1937).

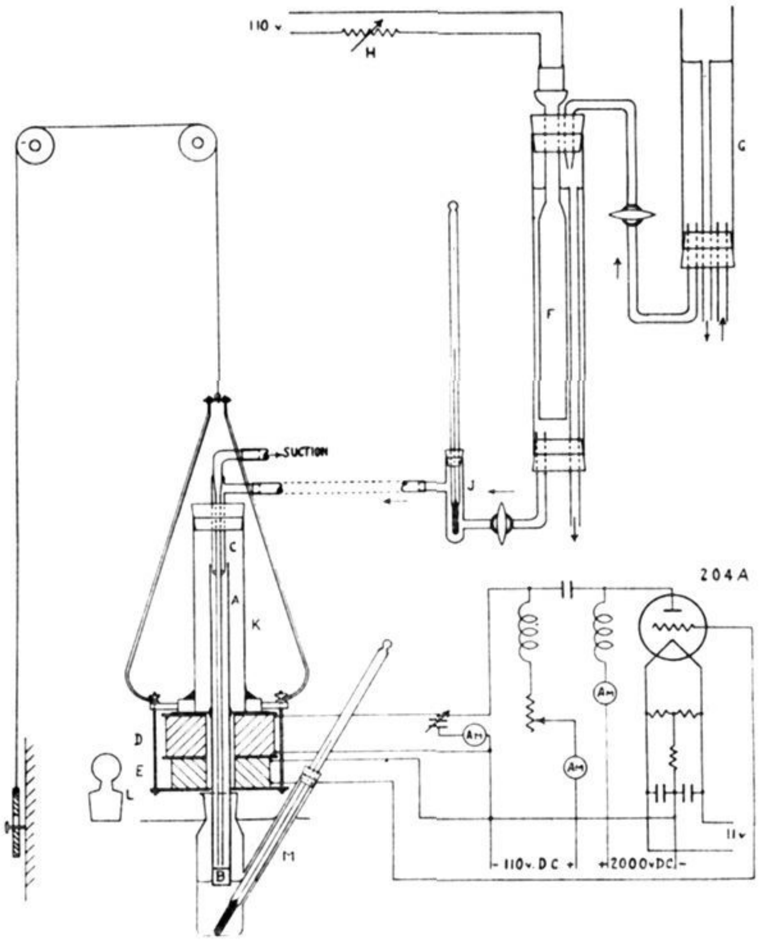

Fig. 1.—Apparatus used in sound experiments.

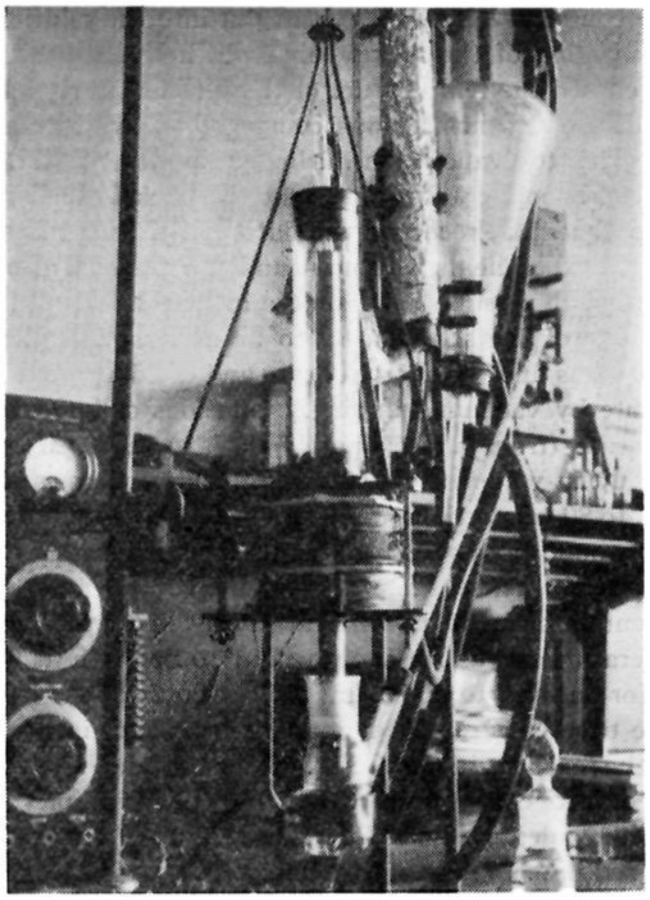

Fig. 1a.

effort was made to maintain constant power input to the coils. The tank current through the driving coil was 0.80 ampere, the polarizing current 1.3 to 1.4 amperes, while the plate current through the amplifying tube was 125 milliamperes.

(3) The nickel tube used was of hard-drawn stock, 30.5 cm. long by 15.9 mm. O. D. and 0.71 mm. wall thickness. A solid plug, B, of molded boron carbide, B_4C, copper plated on one end so that it could be soldered directly to the nickel tube, was used at the lower, closed end of the tube, and thus no nickel came into contact with the solution being studied.

(4) The heating of the nickel tube due to magnetostrictive action was overcome by introducing a spray of water from a glass jet, C, provided with four small holes, inserted into the upper, open end of the tube. The water was removed as fast as it entered by suction applied to a long glass tube reaching to the bottom of the nickel tube. In the sound experiments conducted at 25, 60 and 70° the stream of water was delivered to the nickel tube at a constant pressure and at a controlled temperature by means of the system also shown in Fig. 1. F was a 500-watt knife-type immersion heater suspended in a Pyrex glass tube, which was provided with a constant-level device and was supplied in turn with water at a controllable rate from a second, higher, constant-level device, G, which was connected to a water tap. By variation of the resistance, H, as well as the rate of flow of water, the temperature of the water fed into the nickel tube (read at the point J) could be fixed at the desired value.

(5) The vibrating nickel tube, with its cooling device, and the two coils were assembled in a compact unit (as shown in Figs. 1 and 1a) which could be moved readily up and down by means of a brass "harness," cord and pulleys, so that the liquid to be studied, when placed in a thermostat, could be subjected to vibration for a measured period of time, at the end of which the vibrating assembly could be raised instantly and the solution taken quickly from the thermostat to be chilled and subsequently analyzed. The nickel tube (which vibrated longitudinally) was suspended at its nodal point by means of four thin, narrow, brass strips, silver-soldered to the tube and projecting from it in a plane at right angles to the tube. These supporting strips were separated from the asbestos-covered coils by an insulating plate, and upon the strips was mounted a cylinder of Pyrex glass (46 mm.), K, supported by a fiber collar, which was in turn centered by three fiber rods, threaded to fit holes in the collar and held at their outer ends by brass rods constituting part of the "harness." This Pyrex cylinder was the means of mounting the glass spraying device used to cool the nickel tube in such a way that the nickel tube was completely free of contact with anything except the four brass supports at its nodal point.

The cells containing the solutions to be vibrated were made of 41-mm. Pyrex glass tubing and were fitted with ground glass stoppers, L, so that the concentration of the solutions would not be altered significantly by evaporation during the warming-up period after the cell was placed in the thermostat bath.[8] A 0.1° thermometer was inserted into the oblique side-arm, M, through a small rubber stopper and the temperature of the solution thus could be observed at all times during an experiment. By proper adjustment of the temperature of the cooling water and its rate of flow, it was found possible to maintain the temperature of the solution being vibrated to within 0.1° over the

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[8] Unless the cells were stoppered, the temperature of the solution could not be brought to that of the surrounding bath, due to the cooling effect of evaporation of the water.

entire course of a run. The heat put into the solution by the vibration of the nickel tube, which would otherwise have caused the temperature of the solution to rise above that of the thermostat, was compensated by the cooling effects due to evaporation during the period of vibration and to the cooling water supplied to the nickel tube.

Experimental Procedure without Applied Sound Energy.—In the experiments without sound the rate of hydrolysis of potassium persulfate was determined at 80, 70, and 60°. A sample of the salt, known to be at least 99.6% pure $K_2S_2O_8$, was finely ground in agate and dried at room temperature by vacuum pumping. Solutions of known concentration (from approximately 0.07 to 0.006 *M*) were made up in volumetric flasks and definite volumes (from 25-cc. to 80-cc. portions) were pipetted into tubes provided with ground joints connecting them with small reflux condensers. These samples were introduced at a given moment into an oil thermostat, adjusted to the desired temperature and allowed to warm up to the bath temperature for one-half to one hour. At a recorded time (t_0) one of the tubes was removed from the bath and, in order to stop the reaction, its contents were quickly chilled by being poured into cold water. Similarly other samples were removed at definite times ($t_1, t_2, t_3 \ldots$), and all samples were analyzed immediately after chilling.

The method of analysis employed was with minor alterations that of Kurtenacker and Kubina,[9] to which the reader is referred for more complete details. After the sample was poured into chilled water and the tube repeatedly rinsed, the necessary quantity of phosphoric acid and a measured excess of 0.1 *N* ferrous ammonium sulfate solution (acidified with sulfuric acid) were added and, after a minute's waiting, the excess of ferrous ion was determined by titration with potassium permanganate solution, which had been standardized against sodium oxalate. The normality of the ferrous solution used was determined during the course of the experiment by titration against the permanganate solution, in the presence of phosphoric acid.

From these data the rate constants, *k*, were calculated on the assumption that the reaction is of the first order. Table I represents a summary of the data obtained without the application of sound energy.

TABLE I

RATE OF HYDROLYSIS OF POTASSIUM PERSULFATE WITHOUT APPLIED SOUND ENERGY

Temp., °C.	Concn.	No. detns.	No. runs	k(av.)[a]
79.65	0.0455	3–4	5	0.00514 ± 0.00003
	.0188	3	3	.00587 ± .00007
	.00416	2–3	3	.00658 ± .00004
70.00	.0522	3–4	4	.00161 ± .00001
	.0214	1	4	.00180 ± .00001
	.0141	3	3	.00192 ± .00002
	.00629	1–3	3	.00201 ± .00004
60.00	.0700	1	5	.000413 ± .000002
	.0655	1–3	3	.000425 ± .000005
	.0282	1	6	.000482 ± .000004

[a] When more than one determination of the individual values of *k* for any one solution was made, the average deviation was in general only 1 to 3%.

The energy of activation calculated from these data was found to be 29.1 kcal., independent of the persulfate concentration within the experimental error.

Discussion.—With one important exception, the results of our experiments without the application of sound energy are in reasonable agreement with those of earlier workers, in particular, of Kailan and Olbrich.[3] This point of divergence concerns the constancy of *k* during the period of one experiment. Kailan and Olbrich noted no trend in *k* with time over the interval employed, whereas in our experiments, which extended over much longer periods, a definite increase was observed, particularly in the case of some experiments conducted at 60° for two days. At concentrations approximately corresponding to the lowest cluster of points on the 60° curve in Fig. 2, the values of *k*, determined over a period of from two to six hours on the first day, averaged about 0.00042; whereas, values obtained after the solution had remained in the thermostat overnight ran as high as 0.00048. In the data presented below, all *k*'s represent results obtained during the first few hours after being brought to the designated temperature. In view of these facts, the line of reasoning developed by Kailan and Olbrich to account for their data, based upon the assumption that *k* does not alter with time in one experiment, seems to be invalidated. This reasoning included such assumptions as the retarding action of sulfate and potassium ions, acting in opposition to the accelerating effect of hydrogen ion.

In agreement with these authors, our results show that *k* varies with concentration, as will be seen by reference to Fig. 2, in which *k* is plotted against the average concentration of potassium persulfate at 60, 70 and 80°, for approximately the same percentage hydrolysis. Each cluster of points represents results obtained starting with the same initial concentration.

Experimental Procedure with Applied Sound Energy.—In the case of the experiments conducted in order to ascertain whether or not sound energy produces an intrinsic effect upon the rate of reaction, the number of variables concerned is large and no attempt was made at this time to study the influence of systematic alteration of some of them. It was rather our object to maintain as constant a set of experimental conditions as possible so that any conclusions drawn would be definite. The frequency employed, therefore, was fixed by the use of the same nickel tube throughout the experiments; the same electrical settings ensured reasonable constancy of the power supplied to the coils; and the cells employed were closely similar in size and shape.

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(9) Kurtenacker and Kubina, *Z. anal. Chem.*, **83**, 14 (1931).

Two similar cells, stoppered and supported by spring clamps, were placed simultaneously in the thermostat. One of these cells was removed for analysis at the same moment (t_0) that the vibrator (which had been running for some time previously) was lowered into contact with the solution in a second cell, provided with the side arm and thermometer. The latter cell was removed for analysis at a subsequent time (t) at the same moment that the vibration was stopped. The persulfate content of both cells and the time interval between their respective removals permitted the calculation of the monomolecular rate constant, k, as before.

Separate experiments were conducted to determine the extent of change in concentration due to a slight unavoidable evaporation during the period of vibration, in which the reaction cell was not stoppered. The decrease in k attending this increased concentration could be read off directly from the plot of k *vs.* concentration and thus the comparative, corrected result without sound determined.

The data with applied sound energy are shown in Table II.

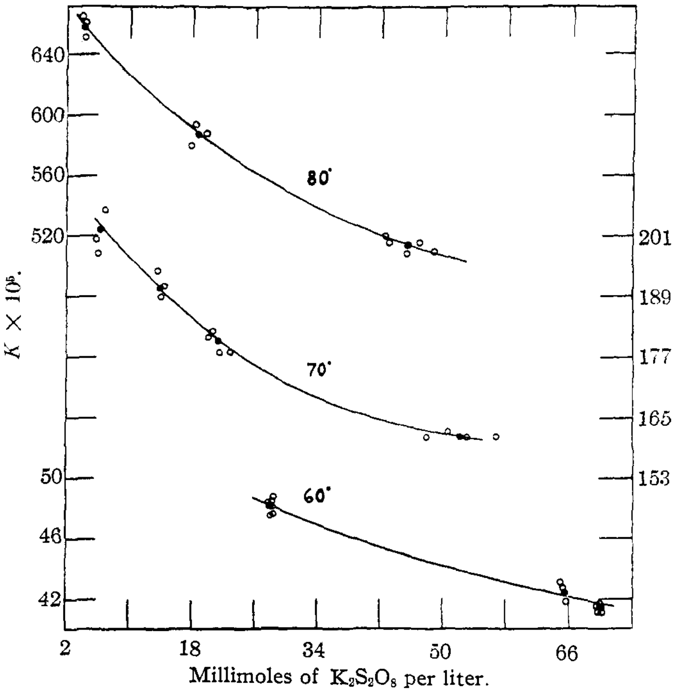

Fig. 2.—Plot of K *vs.* average concentration of $K_2S_2O_8$: ○, run averages; ●, weighted averages.

Discussion.—From the results tabulated above it is to be concluded that, when purely thermal effects are carefully balanced out and any possible catalytic effect of metallic nickel is eliminated, the application of sound energy still has an accelerating influence upon the rate of hydrolysis. Although this effect is doubtless intimately connected with the phenomenon of cavitation, we are not in a position to explain the mechanism by which the result is brought about. Various hypotheses have been advanced from time to time to account for the chemical effects of sound energy, including such ideas as the existence of an electrified layer on the surfaces of the cavitation vacuoles, and the formation of local "hot spots" close to the vibrating tube or at the center of cavitation spaces at the instant of collapse of such cavities.

TABLE II

RATE OF HYDROLYSIS OF $K_2S_2O_8$ WITH APPLIED SOUND ENERGY

Temp., °C.	Time of vibration, hr.	Average vol., cc.	Av. concn., mole/l.	Av. k	k without sound (from plot)	Per cent. increase in k due to sound
70.0	2	63	0.0217	0.00194	0.00180	7.5
60.0	2	59	.0286	.000528	.000480	9.5
60.0	1	59	.0292	.000511	.000479	6.5
60.0	2	24	.0743	.000438	.000413	5.9
60.0	2	24	.0300	.000489	.000477	2.5
Room	2 to 3.3	40 to 60	.0415 to .0182	....	....	0.[a]

[a] No measurable change in persulfate content occurred at this temperature.

In this connection we have conducted explorations with a small, sensitive thermocouple with one junction placed in the liquid immediately below the closed end of the vibrating tube, the other some distance away in the body of the liquid being vibrated, and have failed to observe any appreciable difference in temperature between the two positions. The violence with which the liquid being vibrated is stirred, furthermore, renders it improbable that any such hypothetical "hot spots" could be detected.

It should also be noted in this regard that k increased with increasing volume of solution at the same concentration, as shown by comparison of the results obtained at 60° with 24 cc. and 59 cc. of approximately 0.03 M solution. This result is additional indication that the effects obtained were not due to a "hot spot" in the solution close to the vibrator, as in such a case the volume of solution vibrated should have no effect upon the results; but rather that the added energy was absorbed by the solution as a whole.

The data presented above indicate that when the results are calculated on the assumption that the reaction is monomolecular, k is found to be smaller for shorter times of vibration. At the same volume of solution the effect of sound is greater at the higher concentrations of persulfate.

The relatively great dependence of the effects due to sound upon volume and concentration seems to indicate that in our experiments, at best only a small fraction of the sonic energy applied was actually absorbed by the solutions. Undoubtedly the degree of cavitation attained, and hence the magnitude of the sonic effect upon the rate of hydrolysis, are affected by the shape of the containing vessel, the volume of the liquid, and other factors.

At 25° the rate of hydrolysis, either with or without added vibration, is too slow to be measured over an interval of several hours. At 60° the application of sound energy causes a small but definite increase in the rate of hydrolysis. This acceleration of the rate, expressed as a fractional increase in k, is apparently slightly smaller at 70° (especially in view of the fact that a somewhat larger volume of solution was vibrated in that case). These experimental results are in accord with the following considerations.

Molecules which enter the measured reaction are those which possess an energy equal to or greater than the energy of activation, E. The fraction of molecules in the system which possess this energy derived from thermal energy alone is given approximately by $e^{-E/kT}$, and if energy derived from any other source, E_s, is effective in activating the molecules, then the fraction of molecules with energy E or greater is

$$f = e^{-(E - E_s)/kT} = e^{-E/kT} \cdot e^{E_s/kT} \text{ or } e^{-E/kT}$$

multiplied by a factor which decreases with increasing temperature.

In order to produce a "measurable reaction," the fraction of molecules which possess an energy, E, or greater, must exceed some finite number, depending upon the time interval used to measure the reaction and upon the accuracy of the measurements, because the velocity constant of the reaction is given by the expression: $k = Ae^{-E/kT}$. Therefore, in any case, the effect of sound will not be measurable unless at least this minimum fraction of molecules possesses the energy, E, or greater; but the measurable effect of sound energy, expressed as a fractional increase in k, will be greater, the lower the temperature at which the reaction can be measured.

Summary

1. The rate of hydrolysis of potassium persulfate was studied at 60, 70 and 80° over a wide range of concentration. The results were found to be in substantial agreement with previous work, the monomolecular k decreasing with increasing concentration. One outstanding exception, however, was noted: that k increased with time in the course of a single experiment conducted over a long period.

2. The rate of hydrolysis was studied at 25, 60 and 70° with the application of sonic energy, using improved apparatus. When purely thermal effects were balanced out and any possible catalytic effect of metallic nickel was eliminated, the application of sound energy was found to result in an increase in the reaction rate.

3. The monomolecular k with applied sound energy was found to increase with increased time of vibration, with increased concentration of persulfate, and with increased volume.

4. The effect of sound energy was found to be too small to be measured conveniently at 25°. At 60 and 70° a definite increase in reaction rate was observed, which, expressed as a fractional increase in k, was perhaps slightly smaller at 70°.

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