[CONTRIBUTION FROM THE NAVAL RESEARCH LABORATORY]

Chemical Effect of Ultrasonic Waves: Oxidation of Potassium Iodide Solution by Carbon Tetrachloride

BY ALFRED WEISSLER, HERBERT W. COOPER AND STUART SNYDER

Intense ultrasonic waves produce unusual physical, chemical, and biological effects in liquids. Pioneer work in chemical ultrasonics was done in 1927 by Richards and Loomis,[1] on such effects as the dispersion of colloids and the iodate clock-reaction. Next it was shown[2] that iodine is produced when ultrasound travels through potassium iodide solution containing dissolved air; this was attributed to the formation of hydrogen peroxide from dissolved oxygen, which is activated by cavitation.

Liu and Wu investigated the same reaction,[3] agreed that both oxygen and cavitation are essential, and found that adding a little carbon tetrachloride to the potassium iodide solution greatly increased the amount of iodine liberated. They believed that the carbon tetrachloride reacts with the activated oxygen to give free chlorine, which then oxidizes the potassium iodide. Harvey suggested[4] that electrical discharges at the collapse of cavitation bubbles are responsible for the activation.

Many other laboratories have studied these reactions[5,6,7,8] and also related ones such as the rearrangement of benzazide,[9] depolymerization of polystyrene,[10] and reduction of mercuric chloride by ammonium oxalate.[11] There is general agreement among these investigators on the difficulty of getting quantitatively reproducible results, but not on many of the other experimental facts and interpretations. The present investigation represents an attempt to elucidate further the nature of these processes.

Apparatus

A commercially-available apparatus, the Ultrasonorator, was used in this work. It provides up to 600 watts of electrical energy, at frequencies of 400, 700, 1000 and 1500 kilocycles, which can be fed to a quartz crystal transducer of 38 mm. diameter, immersed in transformer oil. For continuous operation the oil is cooled by circulation through an external refrigerator. The reaction vessel (for example, a large test-tube) is clamped in place in the oil, a few centimeters directly above the crystal source of ultrasound. During irradiation one observes such physical effects as cavitation bubbles, fog, and the liquid fountain, which are shown in a microsecond-flash photograph in Fig. 1. The majority of the experiments to be described were performed at a frequency of 1000 kc.

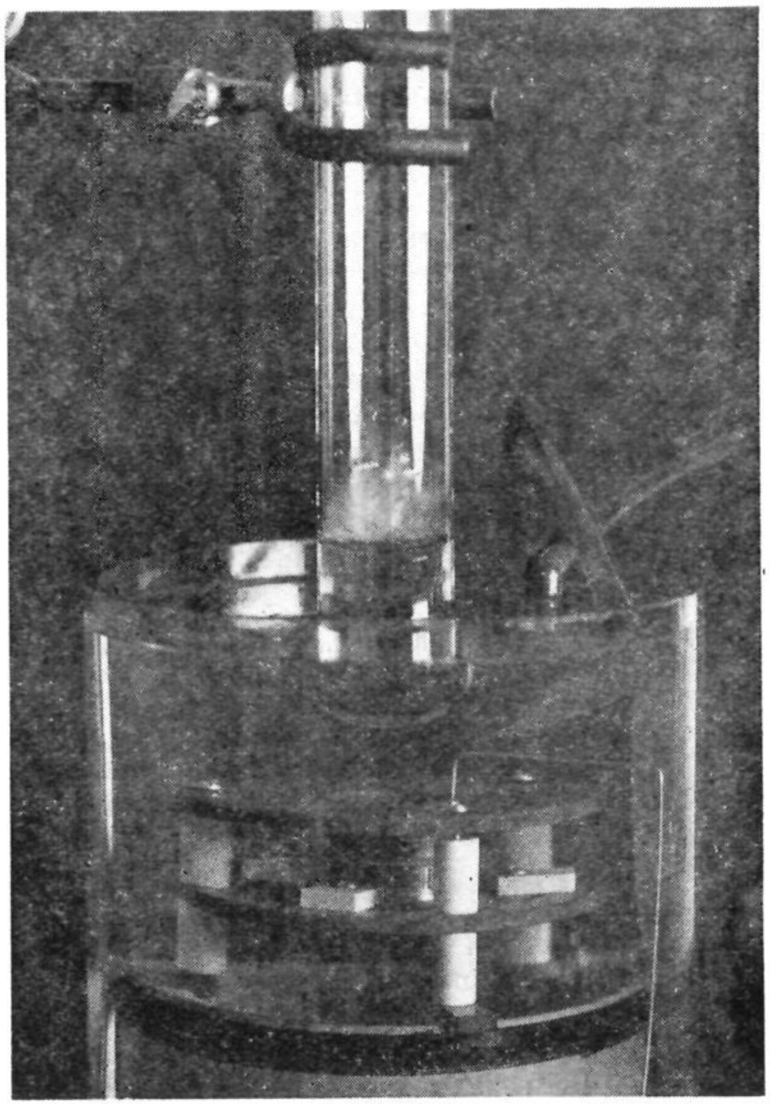

Fig. 1.—Bubbles, fog, and liquid fountain caused by ultrasonic waves.

Physical Background

The energy in an ultrasonic wave is carried through the medium by the back and forth motion of the molecules, which produces alternate compressions and rarefactions. The maximum particle displacement A may be found from the relation $I = 2\pi^2N^2vdA^2$, where I is intensity in ergs/sec./sq. cm., N is frequency, v is velocity of sound in the medium, and d is density of the medium. Applying this, to the specific case of a 1 megacycle wave of 10 watts/sq. cm. intensity in water, shows that the displacement amplitude is very small, less than 10^{-5} cm. However, the acceleration (which is given by $\ddot{x} = 4\pi^2N^2A$) attains very high values, about 250,000 times greater than the ac-

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(1) Richards and Loomis, THIS JOURNAL, **49**, 3086 (1927).

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

(3) Liu and Wu, *ibid.*, **56**, 1005 (1934).

(4) Harvey, *ibid.*, **61**, 2392 (1939).

(5) Bhar, *J. Sci. & Ind. Research (India)*, **1**, 106 (1943).

(6) Flosdorf, Chambers and Malisoff, THIS JOURNAL, **58**, 1069 (1936).

(7) Kling and Kling, *Compt. rend.*, **223**, 1131 (1946).

(8) Sata and Nakasima, *Bull. Chem. Soc. Japan*, **18**, 220 (1943).

(9) Porter and Young, THIS JOURNAL, **60**, 1497 (1938).

(10) Schmid and Rommel, *Z. physik. Chem.*, **185A**, 97 (1939).

(11) Beuthe, *ibid.*, **163A**, 161 (1933).

celeration due to gravity. The maximum instantaneous velocity of the particles is $\dot{x} = 2\pi NA = 40$ cm./sec.

In addition, there are considerable alternations of pressure between compression and tension at a given point in the liquid: $P^2 = 2vld$, where P is the maximum value of positive or negative pressure. For the same wave as before, P is about ±5 atmospheres. One effect of such great changes in pressure is cavitation, which is the formation and violent collapse of small bubbles or voids in the liquid. In the case of water saturated with air, the negative pressure portion of the sound wave (a fraction of an atmosphere is sufficient) causes some of the air to come out of solution as minute bubbles, which then act as weak spots for the further tearing-apart of the liquid to form larger cavities. Then, when the pressure increases, as in the other half of the sound wave cycle, the cavities collapse with a violent hammering action which generates local pressures up to thousands of atmospheres and local temperatures up to several hundred degrees. But if the water is freed from dissolved gases and suspended particles, its apparent cohesive strength is much greater and no cavitation occurs unless negative pressures of the order of 100 atmospheres are applied.

It is in processes such as these that an understanding is to be sought of the characteristic effects of ultrasonic waves.

Experimental Work and Discussion

A quantitative, detailed study of the liberation of iodine from potassium iodide solution by ultrasonic waves was undertaken, with the hope that some of the results would help explain ultrasonic-chemical reactions in general. This oxidation was studied in both the presence and the absence of carbon tetrachloride.

In the absence of carbon tetrachloride, if the oxidation of potassium iodide is brought about by ultrasonically-produced hydrogen peroxide or nitrous acid, then equivalent quantities of free iodine and hydroxyl ion should be formed, according to such an equation as

$$H_2O_2 + 2KI \longrightarrow I_2 + 2KOH$$

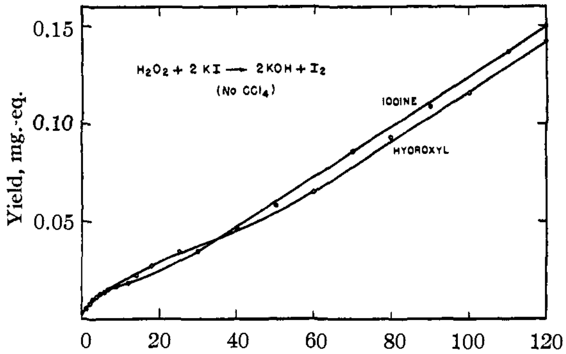

Fig. 2.—Equivalence of hydroxyl and iodine production.

This was verified experimentally by prolonged irradiation at 300 watts input of 100 ml. of 1 N potassium iodide, and continuous titration with both 0.01 N sodium thiosulfate (starch indicator) and 0.01 N hydrochloric acid (brom cresol purple indicator, pH 6.0 at end-point). At the end of two hours about 0.15 milliequivalent, or 20 milligrams, of iodine had been liberated (Fig. 2). The rate-determining step is presumably the "activation" of the dissolved oxygen.

The rate of iodine liberation in the absence of carbon tetrachloride was compared with the rate when carbon tetrachloride was present. Figure 3 shows that the rate is over five times greater when the potassium iodide solution is half-saturated with carbon tetrachloride at the start. If the solution is kept fully saturated by excess carbon tetrachloride, the rate is fifteen times greater than in pure potassium iodide solution.

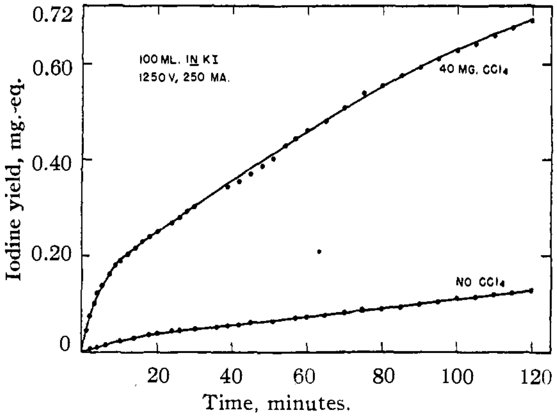

Fig. 3.—Time rate of iodine liberation.

Unless specified otherwise, the remaining work was done using mixtures which contained carbon tetrachloride. Because of the poor reproducibility reported by earlier investigators, the first step consisted of evaluating the effects of certain experimental variables. Experiments were performed at least in duplicate, frequently in quadruplicate.

After reaction vessels made of metal, polythene, porcelain, and glass had been tried, ordinary glass test-tubes were selected as being most suitable

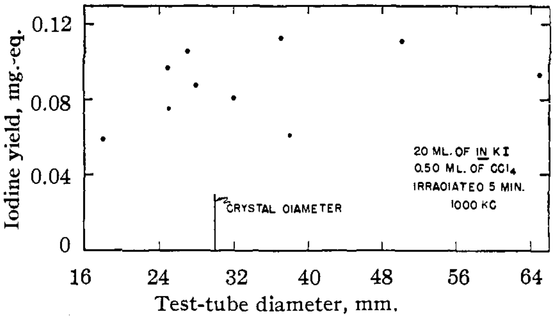

Fig. 4.—Effect of test-tube diameter on yield.

from the standpoint of chemical inertness, availability, and magnitude of yield obtained. Ten different sizes of test-tubes, each containing 20 ml. of 1 *N* potassium iodide and 0.5 ml. of carbon tetrachloride and irradiated for five minutes, gave widely varying results which showed no correlation between iodine yield and test-tube diameter (Fig. 4): it doesn't seem to matter whether the column of liquid is tall and narrow, or short and wide.

However, the yield did appear to be a periodic function of wall thickness of the same ten test-tubes (Fig. 5). This is related to the well-known fact that the sound energy which passes through a barrier is a maximum when the thickness corresponds to an integral number of half-wave lengths.

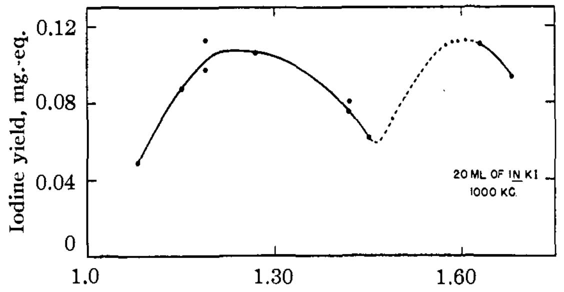

Fig. 5.—Effect of wall thickness on yield.

The 50 × 400 mm. size test-tube was selected as the one to be used in further experiments. Even so, six different test-tubes all of this size gave yields which varied over a range of more than 2 to 1, presumably because of small differences in wall thickness. With high input power, a tube with a very thin glass bottom gave much less iodine (although it transmitted more ultrasonic energy) than a normal test-tube.

It was found necessary to position the test-tube accurately, vertically and horizontally. For example, increasing the distance between the crystal and test-tube caused a considerable reduction in iodine yield because of attenuation in oil (Fig. 6). In addition, small vertical displacements caused large changes in the energy transmitted, because of the effect on the standing wave pattern in the oil; therefore, a screw device was used for fine adjustment to maximum fountain height inside the test-tube.

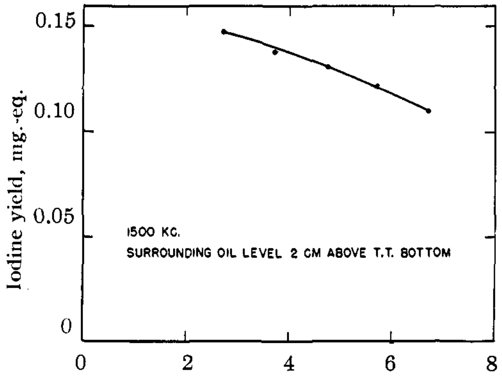

Fig. 6.—Effect of attenuation in oil.

Tight clamping of the test-tube gave a 10% higher yield than loose clamping.

As a result of this preliminary work, by careful control of experimental conditions such as those mentioned, it was possible to attain a reproducibility of between 5 and 10%, which was considered adequate.

It is sometimes argued that the chemical effects of ultrasonic irradiation are due only to the concomitant heating effect. However, this seems unlikely in view of the small temperature coefficient observed by making runs on solutions which had first been brought to temperatures ranging from 2–60° (Fig. 7). In any case, the higher temperatures here give *smaller* yields, probably because of loss of some of the carbon tetrachloride by volatilization. Even if a mixture containing excess carbon tetrachloride is boiled for several minutes, no iodine at all is set free. This demonstrates that it cannot be the generalized heating of the liquid which is responsible for the chemical effect; nevertheless, the possibility still remains that causative factor is the local temperature of several hundred degrees produced at the collapse of cavitation bubbles.

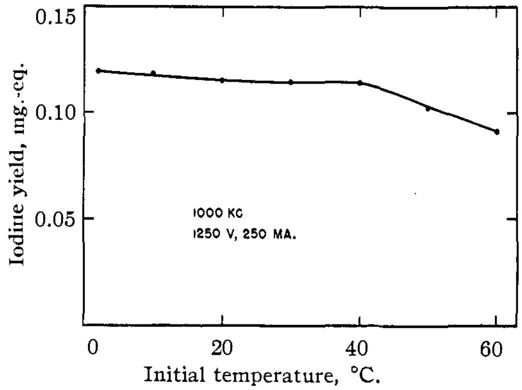

Fig. 7.—Effect of initial temperature on yield.

The variables studied next were those which might give some insight into the mechanism of the reaction. With a constant power input and five-minute irradiation, increasing the volume of potassium iodide solution caused a rapid initial increase in iodine yield up to a broad peak at about 200 ml., and then a gradual falling off at larger volumes (Fig. 8). This indicates that there is an optimum ratio of ultrasonic power to volume of liquid.

If the potassium iodide takes part in the rate-determining step of the reaction, then the rate should be dependent on the concentration of potassium iodide. But experiment revealed that the iodine yield is practically independent of potas-

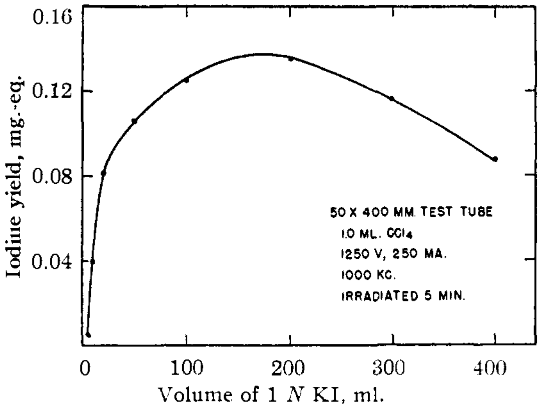

Fig. 8.—Effect of solution volume on yield.

sium iodide concentration over a range of 1000–1 (from 5 *N* down to 0.005 *N*); in extremely dilute solution (0.002 *N*) the yield does drop off (Fig. 9). This shows that the potassium iodide merely indicates the extent of another, more fundamental, reaction which produces oxidizing agents. If enough potassium iodide is present to react with all of the oxidizing agent, it hardly matters how much additional potassium iodide is present.

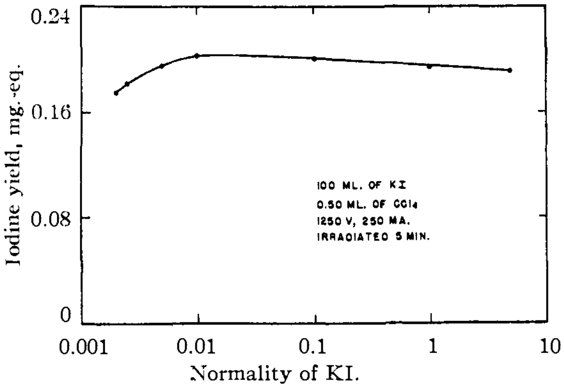

Fig. 9.—Effect of KI concentration on yield.

The amount of carbon tetrachloride used had somewhat greater significance (Fig. 10). Under the specific conditions employed, 0.10 ml was optimum. Larger amounts of this second liquid phase probably cause excessive scattering of the ultrasonic energy and therefore lower yields. Smaller amounts of carbon tetrachloride are used up so rapidly that there is a sharp decrease in iodine liberation.

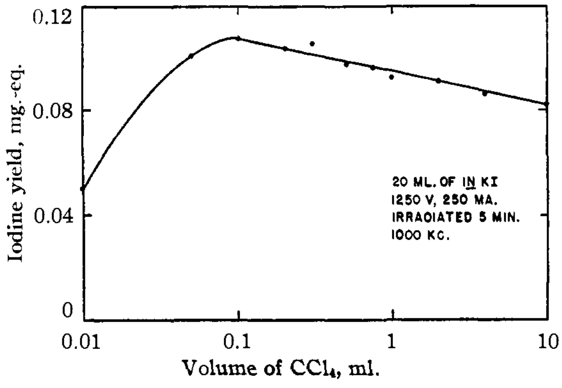

Fig. 10.—Effect of amount of CCl4 on yield.

Increasing the frequency from 400–1500 kc. while keeping constant the power input level, caused an irregular variation in iodine yield (Table I). This is attributed not to intrinsic frequency-sensitivity of the reaction, but rather to varying transparency of the test-tube to ultrasonic energy of different frequencies.

TABLE I

APPARENT EFFECT OF ULTRASONIC FREQUENCY ON IODINE YIELD

100 ml. of 1 *N* KI plus 0.50 ml. of CCl_4 irradiated 5 minutes at 310 watts input in test-tube 3

Frequency, kc.	Iodine produced, equivalent
400	15.7×10^{-5}
700	8.2
1000	15.5
1500	6.5

Next investigated was the manner in which variations of the ultrasonic intensity affect the iodine production, when all other conditions are kept constant. As the power input to the crystal is increased, the yield for a five-minute irradiation increases almost linearly if the volume of solution is large enough (200 ml.), but for smaller volumes (20 or 50 ml.) the yield first increases and then decreases sharply (Fig. 11). This too suggests that there is an optimum energy density: the ratio of power to volume, at maximum yield, is constant for the 20, 50 and 100 ml. solutions.

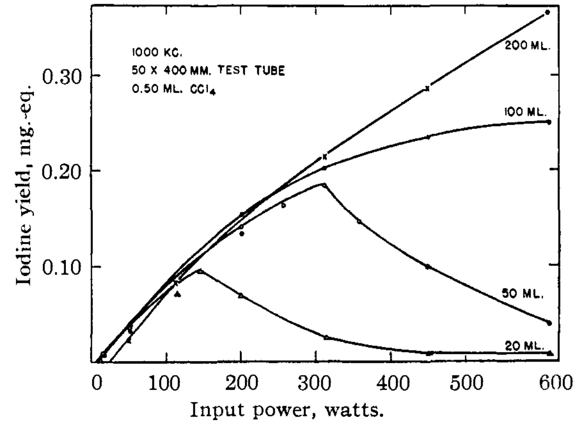

Fig. 11.—Effect of input power on yield.

When the above experiment was repeated at the other frequencies, it was found that the yield at the turnover point for 20 ml., for example, is approximately the same at each frequency; this is another indication that the reaction is not frequency-sensitive. Below a definite threshold power, which coincides with the appearance of cavitation bubbles in the solution, no iodine at all is liberated even after prolonged irradiation. The larger the volume, the greater the power required to produce cavitation and free iodine.

One type of cavitation in a liquid can be produced by a propeller rotating at high speeds, but this kind of cavitation does not cause the oxidation of potassium iodide, even in solutions containing excess carbon tetrachloride. No iodine at all was produced after ten minutes of vigorous cavitation in a Waring Blendor.

Earlier investigators have stated that dissolved oxygen (as well as ultrasonic cavitation) is essential for this reaction. In order to confirm this point, experiments were performed to measure the extent of the reaction when the dissolved gas content of the potassium iodide solution was changed, both in the absence of carbon tetrachloride and with a large excess of CCl_4 (Table II). In the ordinary case where the solution contains dissolved air, the yield corresponds to 1.5 ml. of titrant (0.01 *N* sodium thiosulfate) without carbon tetrachloride and 20.5 ml. with carbon tetrachloride. If the solution is degassed by boiling under vacuum for ten minutes, no iodine is produced upon irradiation, either with or without carbon tetrachloride. If the degassed solution is saturated with either pure oxygen or pure nitrogen, the yields are about the same as for air. This shows that dissolved oxygen is not essential; nitrogen serves nearly as well. (It is known that the oxidant, nitrous acid, is produced by irradiation of water containing nitrogen.) An interesting case is that of helium-saturated solutions where no iodine at all is produced in carbon tetrachloride-free solutions, but in the presence of excess carbon tetrachloride, as much iodine is produced (by irradiation for five minutes) as in air-saturated solutions. This demonstrates clearly that the free chlorine is not liberated from carbon tetrachloride by activated oxygen or similar oxidant, as was stated by previous investigators. There is no reaction between helium and water which could produce such an oxidant. Instead, the carbon tetrachloride itself participates in the primary sonochemical reaction: the carbon-to-chlorine bond is broken by the large mechanical or electrical forces generated at the collapse of cavitation bubbles. (It seems as if only that part of the carbon tetrachloride which is dissolved in the water is available for such a reaction.) Now, in order to facilitate cavitation, some dissolved gas must be present, but it is not necessary for that gas to be oxygen. With carbon dioxide, surprisingly, no iodine is produced either in the presence or absence of carbon tetrachloride.[12]

TABLE II

EFFECT OF DISSOLVED GAS ON IODINE YIELD

100 ml. of 1 *N* KI irradiated 5 minutes at 1000 kc., 310 watts input

Dissolved gas	Iodine yield, equiv. No CCl_4	Iodine yield, equiv. 0.5 ml. CCl_4 added
Air	1.5×10^{-5}	20.5×10^{-5}
Oxygen	1.1	26.0
Nitrogen	1.0	15.0
Helium	0.00	19.0
Carbon dioxide	0.00	0.00
No dissolved gas	0.00	0.00

Next investigated were the details of this sonochemical reaction between carbon tetrachloride and water: how many oxidizing chlorines are liberated per molecule, what is the order of the reaction, etc.? Here it was necessary to use much smaller quantities of carbon tetrachloride, which for convenience and accuracy were added in the form of saturated solution of carbon tetrachloride in water (8 mg. per 10 ml.). Then the reaction mixture was irradiated until the rate of iodine production decreased to the value it would have in the absence of carbon tetrachloride, which meant that all the carbon tetrachloride had reacted. (It was, of course, necessary to subtract from all the titrations a blank, representing the amount of iodine liberated under similar conditions in carbon tetrachloride-free solutions. This *net* yield of iodine was taken as equivalent to the amount of oxidizing chlorine produced.) As shown in Fig. 12, this experiment was performed with three different amounts of carbon tetrachloride—0.8, 4.0, and 8.0 mg.; in each case, the total oxidizing chlorine evolved corresponded closely to four atoms per carbon tetrachloride molecule. Therefore, all of the chlorine in the original molecule is converted ultrasonically into oxidizing chlorine.

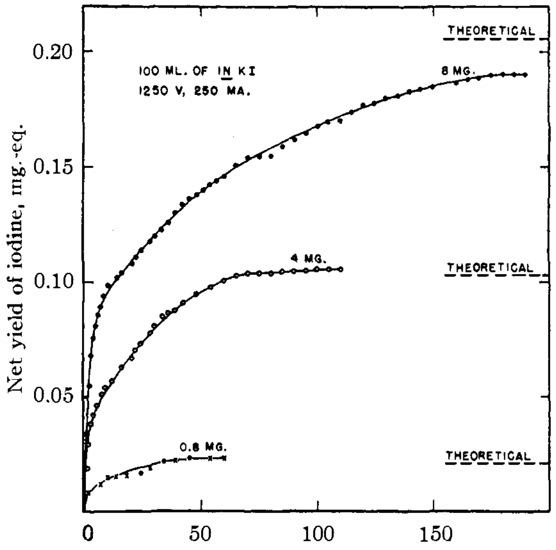

Fig. 12.—Stoichiometric exhaustion of CCl_4.

Inasmuch as the other reactant (water) is present in large excess, it was thought that the kinetics of this reaction might be first-order with respect to

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[12] In this connection, it has been observed that it is practically impossible to obtain standing sound waves in water supercharged with carbon dioxide; see Briggs, Johnson and Mason, *J. Acoust. Soc. Am.*, **19**, 666 (1947).

carbon tetrachloride. Figure 12 shows that it does indeed conform to one of the criteria for first-order: the time required for one-half of the product to be formed is the same (ten minutes) for all three solutions of different initial concentration.

But, for a first-order reaction, plotting the log of concentration of unreacted material against the time should yield a straight line, which is not the case here (Fig. 13). At first there is a sharp drop, then the line is straight between ten and 100 minutes, and beyond that it slopes off gradually. One possible explanation for the initial drop might be a gradual degassing of the solution down to an equilibrium concentration, which would mean a gradual decrease in the amount of cavitation. This hypothesis was disproved, however, by starting with a partly-degassed solution, which was found to give the same sharp initial drop.

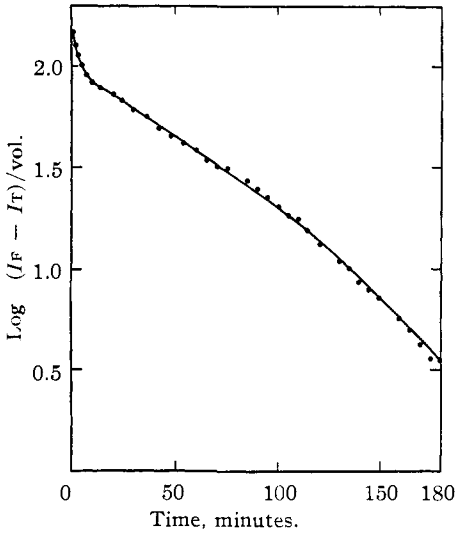

Fig. 13.—Approximation to first-order reaction.

Another possibility was that two consecutive first-order reactions were taking place, the first more rapidly than the second, each producing two oxidizing chlorines per molecule. For constant volume, this may be represented mathematically in the following way.

Let a = initial number of carbon tetrachloride molecules
z = number of carbon tetrachloride molecules which have undergone reaction I by time t
k_1 = specific rate for reaction I
y = number of molecules which have undergone reaction II by time t
k_2 = specific rate for reaction II
c = total number of oxidizing chlorine atoms produced.

Then these differential equations are simultaneously valid

$$dz/dt = -k_1(a - z)$$
$$dy/dt = -k_2(z - y)$$

Solving these, with the ratio k_1/k_2 set equal to 10 for example, yields an expression for the oxidizing chlorines produced

$$c = 4z + \frac{20}{9}(a - z) - \frac{20}{9}(a - z)^{1/10}$$

This theoretical result is compared with the observed rate, in Fig. 14; the abscissas and ordinates have been adjusted by choosing $k_1 = 0.20$ per minute and $a = 0.085$ millimole. It is clear that the observed and calculated rates agree fairly well, but not exactly. Perhaps even better agreement could be obtained by slight changes in the parameters. For the chemical nature of these two consecutive reactions, this tentative proposal is made

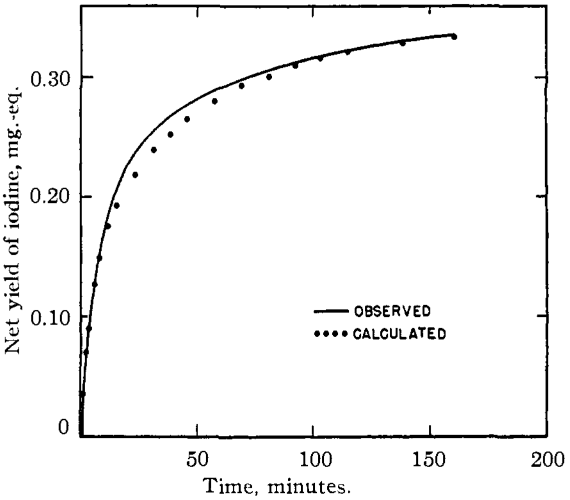

Fig. 14.—Two-step reaction, $k_1 = 10k_2$.

$$CCl_4 + H_2O \longrightarrow Cl_2 + CO + 2HCl \quad (1)$$
$$2HCl + [O] \longrightarrow Cl_2 + H_2O \quad (2)$$

The first might occur through hydrolytic cleavage of one of the C-Cl bonds, followed by disintegration of the resulting unstable trichloromethanol molecule. The second, slower reaction is the oxidation of the hydrogen chloride molecules by some such oxidant as ultrasonically-produced hydrogen peroxide, to give water and another molecule of chlorine.

There is some evidence in favor of this scheme. For example, step 2 was observed to occur independently when a dilute solution of hydrochloric

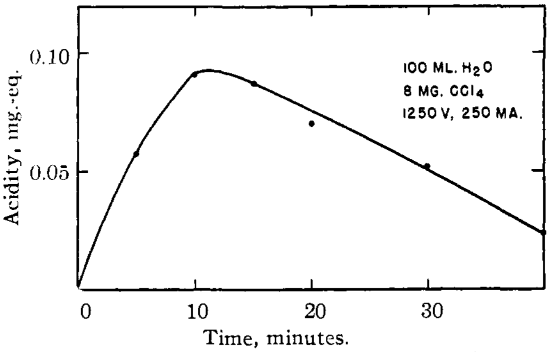

Fig. 15.—Change of acidity with time.

acid was subjected to ultrasonic irradiation. Also, adding excess alkali to the solution, which would prevent step 2, and then irradiating until all of the carbon tetrachloride was exhausted caused the total amount of chlorine produced to be only one-half as great as the normal amount obtained in neutral solution.

A third piece of evidence in favor of the proposed scheme is shown in Fig. 15. The first reaction, which is practically complete in ten minutes, produces hydrogen chloride; the second step destroys it. This implies that the acidity will increase to a maximum value at ten minutes, and then decrease gradually. Such a prediction was confirmed experimentally, by irradiating 8 mg. of carbon tetrachloride in 100 ml. of water. For this case the theoretical maximum acidity is a little over 0.10 milliequivalent; the value observed was a little below 0.10, because some destruction of HCl took place even in the first ten minutes.

However, infrared and mass-spectrometer analyses[13] showed that carbon dioxide is produced, not carbon monoxide, by irradiation of a mixture of water and excess carbon tetrachloride in a closed system from which all of the air has been replaced by helium. The carbon dioxide might arise from hydrolysis of some of the intermediate product phosgene, or else from an ultrasonic reaction between carbon monoxide and water. It was interesting to note that, after a few hours of irradiation, the characteristic odor and color of elemental chlorine were unmistakably present.

Summary

1. The amount of iodine liberated by ultrasonic waves from potassium iodide–carbon tetrachloride aqueous solutions depends on the dimensions and material of the reaction vessel.
2. Although dissolved oxygen has formerly been considered essential, nitrogen or helium are found to serve almost as well.
3. As the power input is increased, no iodine is produced until cavitation occurs. Then the yield increases almost linearly if the volume of solution is large enough, but for smaller volumes the yield first increases and then decreases sharply.
4. The main reaction is that between water and dissolved carbon tetrachloride, the potassium iodide being primarily an indicator of the oxidizing chlorine set free.
5. Rate studies indicate that the reaction takes place in two steps, each of which liberates two chlorine atoms per carbon tetrachloride molecule. The first step is approximately ten times faster than the second.
6. In the absence of carbon tetrachloride the oxidation of potassium iodide solution proceeds only about one-fifteenth as rapidly as in the presence of carbon tetrachloride.

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(13) These analyses were performed by Dr. D. C. Smith of the Naval Research Laboratory and Mr. S. Schuhmann of the National Bureau of Standards, respectively.

[CONTRIBUTION FROM THE MOORE LABORATORY OF CHEMISTRY, AMHERST COLLEGE, AND THE RESEARCH LABORATORY OF GODFREY L. CABOT, INC.]

The Entropy of Adsorbed Molecules

BY G. L. KINGTON,[1] R. A. BEEBE,[1] M. H. POLLEY[1,2,3] AND W. R. SMITH[4]

It is of fundamental interest in a study of adsorption phenomena to investigate the state of the adsorbed phase. Lennard-Jones[5] and Hill[6] have suggested that we may consider two types of motion of adsorbed molecules, one a long range motion in which the molecules move relatively long distances and exchange places, or a more restricted type of motion in which each molecule oscillates laterally about a potential minimum and is thus confined to a particular region of the surface. Two states of adsorbed molecules are then distinguished, a mobile state and a vibrating state.

It is possible to determine the entropy of the adsorbed molecules from experimental data and also to estimate it from statistical considerations of possible models of the adsorbed state. A comparison of the two kinds of data makes it possible to select the model which produces results which most nearly conform to the experimental data.

Such a comparison was carried out by Barrer[7] for the occlusion system, gas–zeolite. Although the process considered is not one of adsorption but rather of solution, the method of statistical mechanical interpretation of the experimental thermodynamic data is similar to that employed in the present study. It is of interest to note that Barrer concluded that the solute molecules (ethane, propane, *n*-butane, hydrogen) approximate closely to three-dimensional oscillators within the framework of the zeolite, and that no large fraction of molecules could possess even one-dimensional translational freedom within the zeolite.

Kemball and Rideal[8,9] have investigated the

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(5) Lennard-Jones, *Trans. Faraday Soc.*, **28**, 333 (1932).

(6) Hill, *J. Chem. Phys.*, **14**, 441 (1946).

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(8) Kemball and Rideal, *Proc. Roy. Soc.* (*London*), **187A**, 53 (1946).

(9) Kemball, *ibid.*, **190**, 117 (1947).