should also be close to the real situation; but a difference plot, such as Figure 6, is quite sensitive to the exact choice of medium-sized basis sets. However, we expect that the transfer of electrons from the oxygen lone pairs to the P–O π bond will show up clearly for any basis set, including an infinite one.

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Chemistry of Ultrasound. I. A Reconsideration of First Principles and the Applications to a Dialkyl Sulfide[1a]

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Abstract: The ultrasonic irradiation of water was effected with 280-, 610-, and 800-kHz transducers at several intensities. Conditions were varied by utilization of different initial pH, temperatures, and gaseous atmospheres in the sealed irradiation vessels. The rate of hydrogen peroxide formation was followed by titrimetric and spectrophotometric analyses. The nature of the gas and the sound intensity were established as the controlling rate factors. Irradiations of carbon tetrachloride in saturated aqueous solutions were accomplished under conditions identical with those applied to pure water. Products included carbon monoxide, carbon dioxide, hypochlorous acid, hydrochloric acid, and hexachloroethane. Product ratios were to some extent intensity dependent. Rates were likewise dependent on intensity but were unaffected by the gaseous atmospheres employed. Di-*n*-butyl sulfide (**1**) was subjected to the standard irradiative conditions while suspended in pure water and in saturated aqueous solutions of carbon tetrachloride. Little rate or product difference was discernible from the two media, or from the change from oxygen to argon atmosphere. The principal product under all conditions was di-*n*-butyl sulfoxide (**2**). Minor products included *n*-butylsulfonic acid (**5**), butyric acid, carbon monoxide, ethylene, acetylene, and methane. The sources of these materials were explored and a mechanistic pathway is presented which accommodates the consolidated information gathered from the irradiations of water and aqueous solutions of carbon tetrachloride and sulfide.

The irradiation of many liquids with ultrasonic waves is known to produce chemical transformations of the liquids and/or of substances dissolved in them.[2] The initiation of these reactions is somewhat speculative, but in most cases seems to be connected to the cavitation of the liquid. Cavitation bubbles, formed by phased temporary reductions of pressure at points in the liquid, are filled with vapor and dissolved gases. Reactions may take place within the cavity in the gas phase, aided by the electrically charged surface of the bubble.[3] An alternate means of initiating reactions occurs *via* high-energy intermediates which are produced from rupture of chemical bonds by the shock wave[4] or thermal gradient[5] upon collapse of these bubbles. The collapse, caused by the next compression phase, is assumed to generate local temperature rises up to 10,000°K[6a] and pressures of several tens of thousands of atmospheres.[3,6b] It is not surprising then that ionization (electron ejection)[7] and homolytic processes are detectable during irradiation.

One of the by-products of ultrasonic irradiation is a luminescence which in water has both visible and ultraviolet components.[8] This is seemingly due to cavitation bubbles with relatively high electric charges on their surfaces,[9] and the resultant electrical stresses.[10] Conflicting views[9,11] exist as to whether "sonoluminescence" is originated by chemical processes, but it is clear that in some cases[9,12,13] the quenching of luminescence by addition of small amounts of substances with high vapor pressures does *not* also quench the chemical reaction.

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(1) (a) Presented in part at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, Abstracts, ORGN 18; (b) Brown University.

(2) The most extensive review of this subject is included in "Ultrasound. Physical, Chemical, and Biological Effects," E. I. El'piner, Ed., Consultants Bureau, New York, N. Y., 1964, p 371.

(3) Y. I. Frenkel', *Zh. Fiz. Khim.*, 14, 305 (1940).

(4) H. B. Briggs, J. B. Johnson, and W. P. Mason, *J. Acoust. Soc. Amer.*, 19, 664 (1947); J. C. Fisher, *J. Appl. Phys.*, 19, 1062 (1948); R. B. Lindsay, *Science*, 20, 409 (1954); W. Guth, *Acustica*, 6, 526 (1956); E. Mundry and W. Guth, *ibid.*, 7, 241 (1957).

(5) D. Srinivasan and L. V. Holroyd, *Phys. Rev.*, **99**, 633 (1955); V. Griffing and D. Setle, *ibid*, 87, 234 (1952); M. E. Fitzgerald, V. Griffing, and I. Sullivan, *J. Chem. Phys.*, 25, 926 (1956); V. Griffing, *ibid.*, 20, 939 (1952); M. Anbar and I. Pecht, *J. Phys. Chem.*, **68**, 1460, 1462 (1964).

(6) (a) B. E. Moltingk and E. A. Neppiras, *Proc. Phys. Soc., London, Sect. B*, 63, 674 (1950); **64**, 1032 (1951); (b) R. Rayleigh, *Phil. Mag.*, 34, 94 (1917).

(7) A. J. Virtanen and N. Ellfolk, *J. Amer. Chem. Soc.*, 72, 1046 (1950); *Acta Chem. Scand.*, 4, 93 (1950).

(8) R. O. Prudhomme, *J. Chim. Phys. Physicochim. Biol.*, 46, 318 (1949); R. O. Prudhomme and R. H. Busso, *C. R. Acad. Sci.*, 235, 1486 (1952).

(9) E. N. Harvey, *J. Amer. Chem. Soc.*, 61, 2392 (1939).

(10) V. L. Levshin and S. N. Rzhevkin, *Dokl. Akad. Nauk SSSR*, 16, 407 (1937).

(11) (a) A. V. Sokol'skaya and E. I. El'piner, *Akust. Zh.*, 4, 288 (1958); (b) R. O. Prudhomme, *Bull. Soc. Chim. Biol.*, 39, 425 (1957); (c) V. Griffing and D. Setle, *J. Chem. Phys.*, 23, 503 (1955).

(12) G. Schmid, P. Paret, and H. Pfleider, *Kolloid-Z.*, 124, 150 (1951).

(13) A. N. Mal'tsev and M. A. Margulis, *Akust. Zh.*, 14, 244 (1968).

It would appear that sonoluminescence is dependent upon attaining a definite threshold lifetime of the cavitation bubble and that this is somewhat longer than the lifetime required for obtaining chemical reactions. Larger amounts of the same quenching liquids, however, prohibit the reactions as well as luminescence. Presumably reaction termination is due to a more thorough invasion of the bubble causing less energetic collapse prior to the approach of the pressure phase.

Much of the same reasoning can be applied to the failure to observe any important chemical reactions from ultrasonic irradiations of many pure organic compounds. Cavitation is usually absent in these liquids due to their high vapor pressures which prematurely collapse the bubbles. This works in opposition to the effect of their reduced tensile strengths which should lead to easier formation of bubbles. The only detailed report of a productive irradiation of pure organic liquids is that by Weissler[14] on the ultrasonic degradations of carbon tetrachloride and acetonitrile at 800 kHz.

As a consequence, most chemical reactions have been effected by ultrasound using water as the solvent (and frequently as the reactant). Cavitation in water is obtained quite easily above a minimum sound intensity characteristic of the frequency,[15,16] temperature,[17] and external pressure.[18] The products of the irradiation, hydrogen peroxide and molecular hydrogen, are seemingly derived from hydroxyl radicals and hydrogen atoms which can be detected as intermediate species. Other intermediates such as hydroperoxide radicals and H_2O_4 have been postulated,[2] but their existence is less certain. Any of these intermediates and products may account for the oxidations or reductions undergone by compounds which are irradiated in aqueous solution.

In order to study some of the more complex reactions of organic molecules under ultrasonic irradiation it seemed advisable to first reconsider the behavior of water under the conditions which we intended to employ—280–800 kHz at 5–11 W/cm^2. This was necessitated by a wealth of contradictory and incomplete information on this subject as well as on the more involved reactions.

Results

Because of reports[11b] that there were profound influences by dissolved gases on hydrogen peroxide production in irradiated water this aspect was first examined. Columns of water 17 cm high and 5 cm in diameter (300 ml) which were saturated with a single gas were irradiated at constant temperature and pH. Sound sources were 800-, 610-, or 280-kHz transducers giving maximum intensities of 11–12 W/cm^2 at the emitting surface. The water was periodically analyzed for hydrogen peroxide concentration by two different spectrophotometric methods. The rates of hydrogen peroxide formation at 20° were obtained from the slopes of linear time *vs.* concentration plots and are tabulated in Table I. Results for each gas are the averages of at least 5 individual runs with a minimum of 17 observations per run. The effects of temperature on the rate of hydrogen peroxide formation were investigated by conducting the irradiation at 42°. (Higher temperatures were avoided owing to the detrimental effects on cavitation and the peroxide.)

Table I. Rate Studies of the Formation of Hydrogen Peroxide from Water by Ultrasonic Irradiation at 20° and pH 7.0

Gas	Frequency, kHz	Intensity, W/cm^2	$k \times 10^6$, mol/(l. min)
O_2	800	9.4	9.8[a]
			7.6
			7.0[b]
			25.9[c]
		11	11.5[d]
		5.7	2.7
	610	8.2	12.9
	280	9.0	16.3
Ar	800	9.4	2.6
		5.7	0.5
	610	8.2	0.1
	280	9.0	3.1
N_2	800	9.4	0.3
Ne	800	9.4	1.3
He	800	9.4	0.4

[a] pH 2.4. [b] pH 12.0. [c] 42°. [d] One-half volume.

As the intermediates of irradiation need not necessarily result in hydrogen peroxide formation, an analysis of the reductive intermediates was undertaken. Dilute solutions of permanganate ion were irradiated under conditions identical with those previously described. Samples were analyzed spectrophotometrically for the conversion to manganese dioxide. The rate of disappearance of permanganate was approximately equivalent to the rate of hydrogen peroxide formation, but occurred rapidly at a temperature (20°) at which the unirradiated reaction between the peroxide and permanganate is ordinarily quite slow.

The luminescence reported to occur during irradiation of water was observed with all saturating gases utilized. Since it was reported[11b,c] that carbon tetrachloride and carbon disulfide enhanced the luminescence while themselves undergoing chemical reactions, this was investigated. In our hands saturated solutions of either compound in water gave *no* visible luminescence when irradiated. Only when additional liquid was added did both mixtures exhibit luminescence and this occurred only at the interface of the two-phase systems.

In order to examine the effects of carbon tetrachloride on hydrogen peroxide production, the nonluminescing saturated solutions were analyzed as described previously for pure water saturated with a single gas. It was found that *no* hydrogen peroxide was formed. Instead, an oxidizing agent was detected which was unreactive toward permanganate but which liberated iodine from potassium iodide solutions treated with the irradiated solution. This material was hypochlorous acid, and upon quantitative study was found to be produced at a rate five times that of hydrogen peroxide formation under identical conditions from pure water. The total acid concentration of the samples was two times the hypochlorous acid concentration and apparently due to concurrent formation of hydrochloric acid in a 1 : 1 ratio with the oxidizing agent. As plots of hypochlorous acid concentration *vs.* time showed small but regularly increasing deviations from linearity

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(14) A. Weissler, I. Pecht, and M. Anbar, *J. Acoust. Soc. Amer.*, **36**, 1208 (1964).

(15) G. Muller and G. W. Willard, *ibid.*, **20**, 589 (1948).

(16) R. M. G. Boucher, *Brit. Chem. Eng.*, **15**, 363 (1970); W. Gaertner, *J. Acoust. Soc. Amer.*, **26**, 977 (1954).

(17) F. G. Blake, *Phys. Rev.*, **75**, 1313 (1949); J. P. Horton, *J. Acoust. Soc. Amer.*, **25**, 480 (1953); A. S. Bebchuk, *Akust. Zh.*, **3**, 90 (1957).

(18) (a) I. G. Polotskii, *Zh. Obshch. Khim.*, **17**, 1048 (1947); (b) cavitation is usually absent in completely degassed liquids.[2]

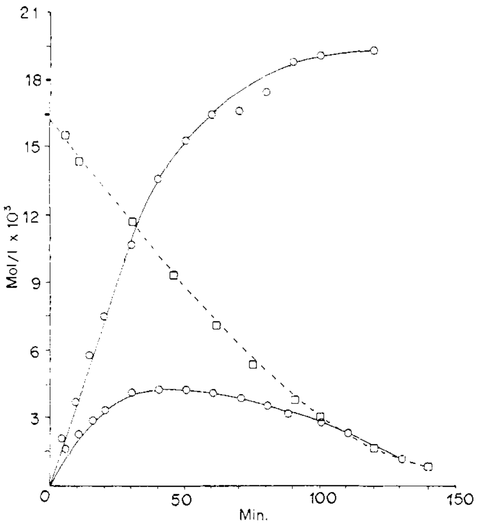

Figure 1. Hypochlorous and hydrochloric acid formation from carbon tetrachloride in saturated aqueous solution, and the decomposition of hypochlorous acid with 800-kHz, 11-W/cm^2 irradiation under argon atmosphere: ⊙, [HCl + HOCl]; □, [Cl_2 − H_2O]; ○, [HOCl].

under an oxygen atmosphere, and larger similarly varying deviations (see Figure 1) under an argon atmosphere, the occurrence of a secondary process—the decomposition of hypochlorous acid to hydrochloric acid and oxygen—was suspect. To examine for this, solutions of chlorine in water were irradiated under conditions identical with those used for carbon tetrachloride studies, and the rate of hypochlorous acid disappearance was followed. The results are tabulated in Table II, and an Ar atmosphere run is shown graphically in Figure 1 along with a run of chlorine water decomposition under identical conditions. The results in argon atmosphere particularly confirm this process as a contributor to the overall product balance (in Figure 1, note the coincidence of hypochlorous acid concentrations with extended time); thus, only the very early phases of the carbon tetrachloride runs were utilized to estimate the rates of hypochlorous acid formation shown in Table II.

Table II. Rate Studies of the Decomposition of Carbon Tetrachloride and Chlorine at 20°, Saturated Water Solution

Gas	Frequency, kHz	Intensity, W/cm^2	$k \times 10^4$ mol/(l. min) HOCl	 HOCl + HCl	 HCl
O_2	800	9.4	1.97	5.22	
		5.7	0.88	1.81	
		9.4[a]	1.86	4.23	
	610	8.2	1.08	2.55	
	280	9.0	1.30	3.60	
Ar	800	9.4	1.63	3.41	
		5.7	0.64	2.08	
	610	8.2	0.70	1.73	
	280	9.0	0.82	4.98	
$Cl_2 + O_2$	800	9.4			0.76
		5.7			0.34
	280	9.0			0.65
Cl_2 + Ar	800	9.4			1.67
		5.7			0.82
	280	9.0			1.55

[a] 41°.

The carbon-containing products of carbon tetrachloride irradiation detected by our methods[19] were carbon monoxide, carbon dioxide, and hexachloroethane. The first two were the only carbon products under an oxygen atmosphere and were detected and analyzed by infrared analyses of the gases expelled during irradiation of the liquid column. An approximate 2:1 ratio of monoxide to dioxide was observed regardless of frequency and intensity of irradiation. Hexachloroethane, which was never detected under oxygen, precipitated from some aqueous solutions irradiated under argon and was collected by filtration and extraction methods. Analyses were conducted gravimetrically, and the proportions of this material relative to the gaseous carbon products were found to be dependent on the frequency and intensity of irradiation. At maximum intensity and frequency (9.4 W/cm^2 and 800 kHz) only carbon monoxide and dioxide were detectable, while for 5.7 W/cm^2 at the same frequency the fraction of these gases was 0.52 and that of hexachloroethane 0.48. Essentially equivalent proportions were found with irradiations at 610 kHz (8.2 W/cm^2) and 280 kHz (9.0 W/cm^2). All three compounds could be shown to be stable to the irradiation conditions; thus, the observed effects must be related to the primary decomposition process of carbon tetrachloride and not to some subsequent phenomenon.

Having, in effect, calibrated the irradiation apparatus with the above described experiments, we turned to the investigation of dialkyl sulfides whose subjection to ultrasound had not been previously reported. Di-*n*-butyl sulfide (**1**) was chosen in particular because of its well-characterized oxidation products, di-*n*-butyl sulfoxide (**2**) and di-*n*-butyl sulfone (**3**). In addition, the probability that any fragmentation products might contain the butyl group was attractive since it maintains a convenient simplicity while enjoying enough characteristic structural features to make identification of its source and fate practical.

Irradiation of the sulfide in 0.006 *M* aqueous suspension at 20° under oxygen or argon atmospheres led principally to sulfoxide **2** (see Table III). Material recoveries were highly variable (50–90%), with the more erratic results obtained under oxygen where a competing polymerization was important. Analyses were conducted by gas chromatography and values reported in Table III are the averages of at least two runs. In order to test the stabilities of the isolated products to the irradiation conditions, the sulfoxide **2** and sulfone **3** were similarly subjected to irradiation in aqueous suspension. In both cases chemical changes could only be practically effected by irradiation at the maximum intensities (11 W/cm^2) which we have employed. The principal product in each case was *n*-butylsulfonic acid (**5**), which is the minor product from irradiation of sulfide **1**. Formation of **5** provoked interest in the gaseous products of irradiation since it was apparent that at least in the case of argon runs the missing butyl fragment was not present in solution. Infrared analyses of the gases above the irradiated columns of water after argon-saturated reactions of sulfide **1** showed the presence of carbon monoxide, methane, ethylene, and acetylene in 8.2:2.5:1:0.7 ratios. The sulfoxide **2** and sulfone **3** gave similar

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[19] It has been reported that tetrachloroethylene is a product of the irradiation of aqueous suspensions of carbon tetrachloride under argon: B. H. Jennings and S. E. Townsend, *J. Phys. Chem.*, **65**, 1574 (1961).

Table III. Product Studies of the 800-kHz Irradiation of Di-*n*-butyl Sulfide (**1**), Sulfoxide (**2**), and Sulfone (**3**) at 20° in 0.006 *M* Aqueous Suspension

Compound	Gas	Intensity, W/cm^2	Time, hr	Relative product ratios			
				R_2S	R_2SO	R_2SO_2	RSO_3H
R_2S	O_2	9.4	19	Trace	85		15
		9.4	15	11	80		9
		9.0	15^a	17	76		7
		9.4	16^b	5	90	Trace	5
	Ar	9.4	16	10	80		10
R_2SO	O_2	11	3.5		85	7	8
	Ar	11	3.5		82	8	10
R_2SO_2	O_2	11	3.5			>99	Trace
	Ar	11	3.5			95	5

^{a} 280 kHz. ^{b} The sulfide was suspended in a standard solution of carbon tetrachloride in water.

ratios of these products, and most important, a control experiment employing *n*-butyraldehyde in aqueous solution also resulted in this ratio of gases (significantly, *n*-butyric acid and *n*-butyl alcohol did *not* give all three products upon irradiation). With oxygen atmospheres, gas was taken up by all of the above compounds rather than evolved and butyric acid was detected in the product mixtures. In another control, *n*-butylsulfinic acid (**4**), prepared by the method of Truce,[20] was irradiated under an oxygen atmosphere and found to rapidly consume 1 equiv of oxygen while converting to the corresponding sulfonic acid **5** with a small amount of polymerization. Under argon a very slow evolution of ethylene and methane was noted, but the major product was again **5**.

Rates of gas consumption and evolution were followed during irradiations by attachment of a gas buret to the apparatus. The results are shown in Table IV.

Table IV. Rate Studies of Gas Consumption and Evolution during 800-kHz, 9.4-W/cm^2 Irradiation of 0.006 *M* Solutions of Di-*n*-butyl Sulfide, Sulfoxide, and Sulfone at 20°

Compound	Gas	Gas consumption $k \times 10^5$ mol/min	Gas evolution $k \times 10^5$ mol/min
n-Bu_2S	O_2	1.73	
	Ar		1.53
n-Bu_2SO	O_2	1.30	
	Ar		1.38
n-Bu_2SO_2	O_2	0.81	
	Ar		1.49
	O_2	0.65	
n-PrCHO	Ar		1.96

The evolution of gases in argon atmosphere runs occurred at the same rate whether the material irradiated was **1**, **2**, **3**, or butyraldehyde. Since these four compounds had been shown to give nearly identical ratios of gaseous products, the intermediacy of the aldehyde in cleavages of sulfide, sulfoxide, and sulfone was implicated. In keeping with the rapid rate of fragmentation shown by the aldehyde, no traces of this compound were found in the solutions during irradiations of the sulfur compounds. The consumption of oxygen, in contrast to the argon results, was quite characteristic of the material irradiated. The rates diminished in the order *n*-Bu_2S > *n*-Bu_2SO > *n*-Bu_2SO_2 > *n*-PrCHO. This was in accord with the results in Table III which indicate that the first oxidative reaction (sulfide to sulfoxide) is much preferred over the second (sulfoxide to sulfone) and subsequent oxidative processes.

Discussion

The close relationship between the nature of the gaseous atmosphere and the rate of hydrogen peroxide production from pure water was, as mentioned, not unexpected. Nevertheless, a marked difference from previous reports[11b] was observed. In our case, the magnitude of the rate was inversely proportional to the ionization potential of the gas (admittedly the effects of oxygen and nitrogen may be more complicated than the rest due to the reactions of these molecules with the intermediates of peroxide formation[21]). Inspection reveals, in fact, a near-quantitative relation between the rates of hydrogen peroxide appearance and ionization potentials of oxygen (12.5 eV), argon (15.7 eV), neon (21.5 eV), and helium (24.5 eV). The solubilities of the gases in water, a reportedly[11b] strong influence,[22a] had no discernible effect in our experiments. If theories[22b] on the degassing effects of ultrasound are correct, the amounts of gas actually in solution should be small for all of the gases examined, and the differences in their concentrations therefore minimal. Ultimately, the conclusion must be that ionization of the gas within the cavitation bubbles is the initiating and rate-controlling step for the conversion of water to hydrogen peroxide *via* hydroxyl[23] and hydrogen[23] radicals.

The initiation of carbon tetrachloride decomposition likewise seems obvious from the available results (Table II). The essentially temperature-, gas-, and frequency-independent initial rate of hypochlorous acid formation is consistent with the idea that a dissociation to chlorine and trichloromethyl radicals (eq 1) is the first process. Whether the energy for this scission is electrical (from a discharge within the cavitation bubble) or thermal (from the collapse of the cavitation bubble) is not clear, as the strict dependence only on the sound intensity simply implies that cavitation is necessary.[19] The ability of an oxygen atmosphere to divert all carbon-containing intermediates to carbon monoxide or dioxide does, however, suggest that these intermediates may exist in the gaseous environment within the bubble.

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(20) W. E. Truce, D. P. Tate, and D. N. Burdge, *J. Amer. Chem. Soc.*, **82**, 2872 (1960).

(21) M. DelDuca, *et al.*, *J. Acoust. Soc. Amer.*, 30, 301 (1958).

(22) (a) The specific heats and thermal conductivities of gases have also been suggested as influential in determining the rates of ultrasonic reactions; see ref 1, p 21; (b) A. V. M. Parke and D. Taylor, *J. Chem. Soc.*, 4442 (1956).

(23) A. Weissler, *J. Amer. Chem. Soc.*, **81**, 1077 (1959).

$$\mathrm{CCl_4 \longrightarrow \cdot CCl_3 + \cdot Cl} \tag{1}$$

$$\mathrm{\cdot CCl_3 \longrightarrow :CCl_2 + \cdot Cl} \tag{2}$$

$$\mathrm{:CCl_2 + H_2O \longrightarrow CO + 2HCl} \tag{3}$$

$$\mathrm{\cdot CCl_3 + \cdot OH \longrightarrow HOCCl_3} \tag{4}$$

$$\mathrm{HOCCl_3 \longrightarrow COCl_2 + HCl} \tag{5}$$

$$\mathrm{COCl_2 + H_2O \longrightarrow CO_2 + 2HCl} \tag{6}$$

$$\mathrm{\cdot CCl_3 + \cdot O{-}O\cdot \longrightarrow \cdot O{-}OCCl_3} \tag{7}$$

$$\mathrm{\cdot O{-}OCCl_3 + H_2O \longrightarrow COCl_2 + HOCl} \tag{8}$$

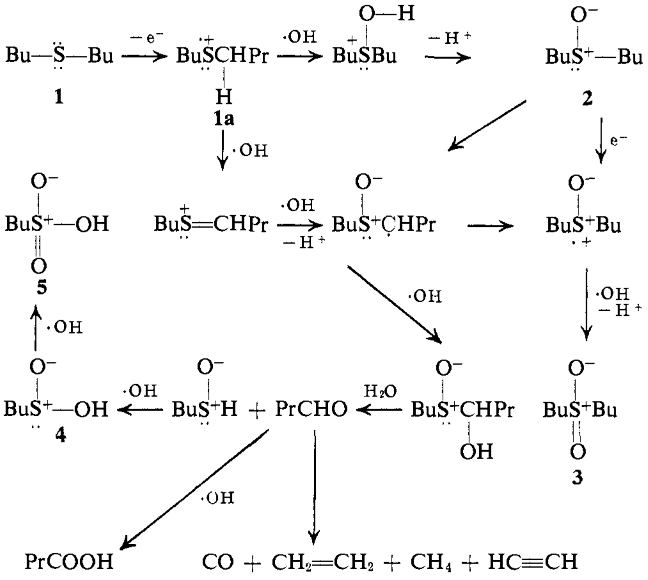
$$\mathrm{\cdot CCl_3 + \cdot CCl_3 \longrightarrow C_2Cl_6} \tag{9}$$

The fate of the trichloromethyl radical is intriguing since it is not only a function of the gaseous surroundings but of the intensity of irradiation when the gas is inert. In the presence of oxygen the coupling reaction (eq 9) is seemingly overcome by the normal tendency to form carbon monoxide (eq 2 and 3) and dioxide (eq 4–6) in combination with the "trapping" effect of molecular oxygen (eq 7 and 8). Removal of the latter possibility by use of argon equalizes the competition between the two routes for trichloromethyl radical except at the highest intensity employed. Here a shift away from the coupling process by the production of a higher energy carbon tetrachloride species, hence trichloromethyl radical, is the logical explanation for the absence of hexachloroethane as a product. We theorize that this more indiscriminate radical will show a greater tendency to decompose or react with solvent-derived species than to couple.

In order to maintain a consistent mechanistic picture when deducing the initiation step of the sulfide oxidation and its place of origin, it is necessary to utilize the prior deductions as to the same features of hydrogen peroxide production and carbon tetrachloride decomposition. As in the latter case, the minimal influence on the rate by changing from oxygen to argon atmosphere suggests that the rate-controlling process involves a direct conversion of the reactant, rather than a transfer of excitation from the ionized gas to sulfide or water. More indication in this respect comes from the irradiation of the sulfide in a saturated aqueous carbon tetrachloride solution (Table III). The slight rate enhancement exhibited under these conditions in no way matches the rapid rate at which carbon tetrachloride is converted to the oxidizing agent, hypochlorous acid (Table II). This change in conditions in fact had remarkably little effect on the sulfide oxidation, and removed any notion that carbon tetrachloride could be used to intensify the effects of irradiation. Having thus eliminated the formation of hydrogen peroxide or hydroxyl radicals as rate controlling and noted the ineffectiveness of the introduction of chloride radicals, the ionization of sulfide (**1** → **1a**) is the likely choice for the initiation step. As before, there is no certainty of the place of this electron ejection, but it does seem that the electrical discharge within the cavitation bubble is an attractive energy source. The further reactions of the ionized sulfide **1a** with hydroxyl radical (Scheme I) to give the sulfoxide can occur either in the bubble or in solution. A similar initiation step is envisaged for the conversion of sulfoxide **2** to sulfone **3**. In this instance, the inherent difficulty in electron removal from the already electron-deficient sulfur, working with the decreased vapor pressure of the sulfoxide (which would limit diffusion into the cavitation bubble), serves to make the reaction quite slow.

The origins of the minor products, *n*-butylsulfonic acid (**5**), butyric acid, ethylene, acetylene, methane, and carbon monoxide, can most easily be attributed to reactions of ionized sulfide **1a** with hydroxyl radicals in solution. An overall pathway is proposed in Scheme I which includes all products of irradiation and their possible (if not in all cases detectable) precursors. Analogies for most of the indicated transformations exist in the solution chemistry of sulfide[24, 25] or sulfonic acid[25a] oxidations. The rapid fragmentation of butyraldehyde has not been reported previously in the literature of ultrasound, but it does bear a resemblance to electron impact behavior during mass spectrometry of this compound.[26] One may suspect that electron ejection is again important in initiating the fragmentation; however, this awaits confirmation by studies currently in progress.

Scheme I



In summary, the application of logic based on the principles of solution and gas-phase systems seems to provide the simplest means by which the mechanistic aspects of transformations caused by ultrasound may be understood. We have in this first report attempted to verify and correlate information on irradiations of simple molecules in order that further work with more complex materials will be comprehensible. The ultimate goal is the achievement of a greater level of predictability and reproducibility for ultrasonic reactions. As the latter aspect has historically been a problem in this area, we have deliberately chosen commercially available sound generators and sources (see Experimental Section) and an uncomplicated irradiation apparatus design in an effort at standardizing conditions. In this manner we believe that the results we describe in this and future papers will be available to others with a minimum of effort.

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(24) C. E. Griffin and K. R. Martin, *Chem. Commun.*, 154 (1965).

(25) (a) J. S. Showell, J. R. Russell, and D. Swern, *J. Org. Chem.*, 27, 2853 (1962); (b) T. J. Wallace, H. Pobiner, F. A. Baron, and E. Schreisheim, *ibid.*, 30, 3147 (1965).

(26) See H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, San Francisco, Calif., 1964, p 3.

Experimental Section[27]

Irradiation of Water. The water for irradiation was purified by distillation from a concentrated aqueous phosphoric acid solution. Before distillation, the system was purged with steam and then filled with an atmosphere of the appropriate gas. The water was then distilled directly into the reaction vessel. By this method water was obtained at pH 7. For runs at pH 2.5, a 0.01 *N* hydrochloric acid solution was made up, and for pH 12 a 0.01 *N* sodium hydroxide solution was used.

Water samples of 300 ml were enclosed in the reaction vessel and placed into the cooling jacket mounted on a transducer. While maintaining the temperature at 20 or 42° the water was irradiated at 800, 610, or 280 kHz with an intensity of 5–11 W/cm^2 within the irradiation vessel. The durations of the runs were from 1 to 2 hr. Aliquots were taken from the reaction vessel at 5-min intervals for hydrogen peroxide analysis. The rate of hydrogen peroxide formation was followed by two colorimetric methods which agreed excellently at pH 7.

Method A. The concentration of hydrogen peroxide in water was followed by the triiodide anion method.[28]

Method B. Because the triiodide procedure was unreliable at high or low pH, the concentration of hydrogen peroxide was determined for solutions at pH 12 and 2.5 by following the change in concentration of aqueous potassium permanganate solutions spectrophotometrically. A sample of water (1–3 ml, depending on the hydrogen peroxide concentration) was added to 2 ml of a $KMnO_4$ solution (8.92×10^{-4} *N*) and 2 ml of 4:1 aqueous sulfuric acid in a volumetric flask. Distilled water was added to bring the volume to 10 ml. The samples were placed in a 1-cm absorption cell and the absorbances were determined spectrophotometrically at 525 mμ. The hydrogen peroxide concentration can be determined by $A_b - A_s = A_d$, where A_b is the absorbance of 2 ml of stock $KMnO_4$ solution and 1 ml of unirradiated sample diluted to 10 ml, and A_d is the change in absorbance. The hydrogen peroxide concentration was obtained by comparison of absorbances with a Beer's law plot for $KMnO_4$.

Irradiation of Carbon Tetrachloride–Water. The water was purified by the previously described procedure and then saturated with carbon tetrachloride at room temperature. The reaction vessel was filled with 300 ml of this solution and irradiated for 1–2 hr under conditions identical with those described previously. Two aliquots of 1 ml were taken at 5-min intervals. One aliquot was analyzed by titration with standard sodium thiosulfate solution of iodine liberated from potassium iodide.[28] This method gave the concentration of hypochlorous acid formed. The second aliquot was titrated with standard sodium hydroxide to a phenolphthalein endpoint. In this manner the total acid concentration was measured. The rate of gas evolution was followed by connecting the gas outlet fixture of the irradiation vessel to a gas buret. Measurements were taken at 5-min intervals. Analyses of gas composition were effected in separate runs where an evacuated infrared gas cell was attached through tubes containing drying agent to the irradiation vessel. The composition was obtained from comparison with previously prepared concentration *vs.* absorbance plots for both gases. Hexachloroethane determinations were effected by filtration of the irradiated liquid followed by careful extraction of the filtrate with chloroform. The residues were analyzed gravimetrically.

Irradiations of Sulfur Compounds or Butyraldehyde in Water. To 300 ml of water purified in the previously described fashion was added enough material for irradiation to bring the suspension or solution to 0.006 *M*. A positive flow of the saturating gas was maintained during the addition of the organic compound in order to avoid the simultaneous admission of air to the apparatus. Rates of gas evolution or consumption were followed as described for carbon tetrachloride runs. Analyses of gaseous mixtures were again by comparison of the infrared absorption with plots of known concentrations of each gas *vs.* infrared absorbance. After filtration to remove any solid polymeric material from the irradiated liquid (no more than 10% of the original material, by weight, was ever found), the solutions or suspensions were saturated with salt and subjected to continuous ether extraction for at least 24 hr. Drying and concentration of these extracts afforded the residues which were examined directly by gc. *n*-Butylsulfonic acid was separated for identification purposes from the other products by extraction of an ether solution of the residues with aqueous sodium bicarbonate. Isolation was accomplished by acidification of the aqueous solution and reextraction with methylene chloride.

Irradiations of Di-*n*-butyl Sulfide in Carbon Tetrachloride Saturated Aqueous Suspension. The procedure was the same as that described previously for irradiations of the sulfide in pure water, except that stock saturated aqueous carbon tetrachloride solutions were used. Analytical methods were identical with those previously applied.

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(27) Irradiations were conducted with a Macrosonics Multisons 100-1 broad-band generator. Actual sound sources were cobalt barium titanate transducers, Model HFS-804, operating with maximum efficiency at 800 kHz with a rated average power output of 85 W, and lead zirconate titanate transducers, Models HFS-570 and HFS-250, operating with maximum efficiencies at 610 and 280 kHz, respectively, with rated average power outputs of 60 W. The irradiation vessel consisted of a cylindrical glass tube, 5 cm i.d. × 17 cm high, to which was affixed, at the lower end, a disk of 500D Mylar film serving as the sound-transparent bottom, and, at the upper end, gas inlet and outlet fixtures for control of the internal gaseous atmosphere. The vessel was fitted to an external cooling jacket by means of standard ground-glass joints which also served to maintain a reproducible distance between the surface of the transducer and the bottom of the vessel (approximately 1 cm). Sound coupling between source and vessel occurred through the water in circulation through the cooling jacket. Relative intensity measurements were made with a Macrosonics cavitation meter, Model CVM-3a. Actual intensity was estimated from the rated average output of the transducers at maximum efficiency. Spectrophotometric measurements were accomplished with a Bausch and Lomb Spectronic 20. Infrared analyses were effected with a Perkin-Elmer Model 237B grating infrared spectrophotometer, and gc analyses accomplished with a Perkin-Elmer F-11 gas chromatograph with hot-wire detector and linear temperature programmer. Columns and conditions employed were 1 ft × $^1/_4$ in. 10% carbowax 20M Chromosorb W, 60–80 mesh, programmed from 70 to 130° at a 40°/min rise and a flow rate of 50 ml/min. The carbon tetrachloride irradiated was reagent grade and used directly. Crystalline di-*n*-butyl sulfone was also used without further purification. Di-*n*-butyl sulfide was freshly distilled before irradiation, as was butyraldehyde, after liberation from its bisulfite adduct. Di-*n*-butyl sulfoxide was crystallized from hexane prior to use.

(28) A. O. Allen, C. J. Hochanadel, J. A. Ghormley, and T. W. Davis, *J. Phys. Chem.*, **56**, 575 (1952).