by the essentially identical value of log k_1 found[23] when Mn-AMP was studied in 99.8% D_2O medium.

The formation constants of the four complexes described in this section, using the ion-exchange method, agree closely with the values obtained using the pH method. Since the difference in the metal ion concentration used in the two methods is clearly very great, the agreement must mean that these complexes are mononuclear.

Acknowledgment.—The authors are indebted to Mr. R. Scrugg and Miss P. Tang for assistance in carrying out the ion-exchange experiments.

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THE SONOCHEMICAL REACTIONS OF CARBON TETRACHLORIDE AND CHLOROFORM IN AQUEOUS SUSPENSION IN AN INERT ATMOSPHERE

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The sonochemical reactions of CCl_4–H_2O mixtures in an argon atmosphere have been investigated and compared with those of $HCCl_3$–H_2O mixtures. The observed products from the CCl_4 reaction were CO_2, O_2, Cl_2, HCl, C_2Cl_6 and C_2Cl_4. After an initiation period, the rates of formation of certain products were found to be constant: $d(Cl)/dt = 9.6$ μequiv./min.; $d(C_2Cl_6)/dt = 4.2$ μmoles/min. (20°); the rate of production of C_2Cl_4 was an order of magnitude slower; the elemental Cl_2 concentration remained essentially constant after the first half hour of reaction. After the initial period, the rate of production of inorganic chlorine was insensitive to a 15° temperature change. The products identified from the $HCCl_3$ reaction were HCl, C_2Cl_6 and C_2Cl_4: $d(Cl)/dt = 4.1$ μequiv./min. (20°). Some interrelationships between cavitation and chemical reaction are discussed. A free radical mechanism is proposed to account for the rate data and observed products.

Introduction

In 1927 Richards and Loomis[1] conducted a preliminary experimental survey of the chemical effects of high frequency sound waves. Since that time many chemical reactions have been observed to occur in an ultrasonic field.[2] Addition, hydration, hydrolysis,[3] decomposition,[4] oxidation,[5] reduction,[6] and rearrangements[7] are among the types of reaction reported to be initiated or accelerated by ultrasound. Polymerization[8] and depolymerization[9] reactions also have been investigated under various conditions.

Recently there have been several successful attempts to interpret experimental results on the basis of free radical reaction mechanisms.[10–13] This suggests the possible use of ultrasound as a means of generating free radicals at room temperature.

In order to gain further insight into the nature of ultrasonic reactions, we investigated the effects of ultrasonic energy on a relatively simple system, carbon tetrachloride–water in an inert atmosphere. Although mixtures of CCl_4–H_2O, with added KI, were among the first to receive attention in ultrasonic chemistry,[11,14] the reactions of CCl_4 alone in aqueous suspension have been the object of but little research. It has been recognized[15–16] that oxidation occurs, but mechanistic studies, in the absence of air, have never been made. We have attempted to characterize all the products generated when CCl_4–H_2O mixtures are ultrasonorated and have followed the rate of production of some of the major components. We have compared these results with those obtained from $HCCl_3$–H_2O under the same reaction conditions. Such analyses should increase our understanding of the nature of the reaction intermediates.

Experimental

Apparatus.—Cylindrical glass vessels, 8″ long and 2″ in diameter, used for all rate experiments, were furnished with essentially sound transparent bottoms made of 50 gauge Saran (Dow Chemical Co.). Each vessel top was provided with a gas outlet tube, an inlet tube and a thermometer; the latter two were raised above the liquid surface during ultrasonic runs to minimize non-reproducible sonic reflections. Glass bottomed vessels were used for runs on which qualitative tests for CO_2 and O_2 were made.

The source of sound energy for most of the experiments

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was a Birtcher Medical Ultrasonic Generator, Megason Model 110, modified to by-pass the timer. This unit operates at a frequency of 1 mc./sec. with a rated electrical output of 15 watts (3 watts/cm.^{2}). The corresponding acoustical power inside the reaction vessel was 6.1 watts as measured by substitution calorimetry.[17] The runs used for CO_2 and O_2 analyses were carried out on a more powerful General Electric Ultrasonic Generator, Model GEI-29578, 300 kc./sec., 75 ma. plate current; acoustical power received by the reacting solution through glass bottomed vessels, 5.0 watts.[17] It was established by experiment that the difference in frequency between the two units did not affect the nature of the products.

Procedure.—Before use, distilled water was boiled for at least an hour and aspirated ($\sim$2 cm. Hg) for at least 45 min. 99.99% pure commercial argon (Linde Air Products), further purified by passage through a train containing Fieser's solution,[18] saturated lead acetate solution, and Ascarite, was used to pump the deaerated water through a suitable pipet into the reaction vessel from which air previously had been swept by a stream of argon.

Spectroscopic or analytical grade CCl_4 and $HCCl_3$ (Matheson, Coleman and Bell) were deaerated by boiling just prior to use, rapidly cooled to 20°, and added by pipet through a capillary adapter to the water in the reaction vessel while a continuous flow of argon saturated the system. Inlet and outlet tubes were closed and the vessel seated directly on the quartz transducer in a thermostated water-bath, a thin layer of water serving as a coupling liquid. Reactions were allowed to proceed for time periods from 15 min. to 3 hr.

Analytical. (A) **Trichloroacetic Acid and Chloroform.**—The reliability of Fujiwara's colorimetric test[19] for $HCCl_3$ and hydrolytic precursors thereof was confirmed using a series of known mixtures. Reported sensitivity is 1 p.p.m. $HCCl_3$ in H_2O. Twelve ml. emulsified reaction mixture was treated with 6 ml. of 10% NaOH and 4 ml. of colorless pyridine.

(B) **Oxygen.**—The gas above the reacted mixture was displaced by means of deaerated water into a basic pyrogallol solution[20] prepared and protected under argon.

(C) **Carbon Dioxide.**—Gas above the reacted mixture was displaced by means of deaerated water into a $Ba(OH)_2$ solution protected by an argon atmosphere. The base was was also added directly to the ultrasonorated mixture.

(D) **Hydrogen Peroxide.**—Titanium sulfate served as a sensitive reagent for determination of H_2O_2.[21] 0.3 ml. of titanium solution[21b] was added, with thorough mixing, to 3 ml. of aqueous reaction mixture and the % T at 410 mμ was read on a Beckman DU spectrophotometer (1 cm. cells) against a blank of untreated reaction mixture. This procedure also served as a check that the water used had been thoroughly freed of air; traces of nitrites formed during ultrasonic reaction[5a] caused the Ti–H_2O_2 complex to fade rapidly. The precision of this colorimetric method is approximately 0.1% as estimated from standard curve determinations with samples of known H_2O_2 concentration. The results from ultrasonic runs used to obtain the rate constant for peroxide production were reproducible within 3%.

(E) **Total Inorganic Chlorine.** (1) **CCl_4 Reactions.**—*Ca.* 5 ml. of 6 *N* NH_4OH was introduced directly into the reacted mixture,[22] the closed vessel agitated and the fumes allowed to settle before transference to an erlenmeyer flask. Additional NH_4OH was put in to repress hydrolysis of the NH_4Cl, the solution evaporated to a suitably low volume and diluted quantitatively to 100 ml. Aliquots were titrated with standard 0.01 *N* $Hg(NO_3)_2$ solution using diphenylcarbazone-brom phenol blue mixed indicator.[23] (2) **$HCCl_3$ Reactions.**—After the ultrasonorated emulsion had separated, 5-ml. aliquots were withdrawn directly from the aqueous phase and titrated as above.[23] Determination of Cl^- with $Hg(NO_3)_2$ is precise to *ca.* 0.1%; greater error attended the analyses of ultrasonic runs: values averaged for calculation of rate constants were within 10%.

(F) **Elemental Chlorine.**—The pale yellow CCl_4 reaction mixture was agitated to redissolve any Cl_2 which may have been ultrasonically expelled from the liquid. The whole then was titrated, after transference to an erlenmeyer containing excess KI, against standard 0.01 *N* $Na_2S_2O_3$ using the CCl_4 as the indicator. The titration is precise to at least 0.1%; analyses of ultrasonic runs were within 4%.

(G) **Total Acidity.**—(H^+) was determined by titration with standard base. Error in results paralleled the error for chloride determination.

(H) **Organic Constituents.**—C_2Cl_6 was isolated many times from the organic layer as a pure white solid; m.p. 186.9–187.4° in a sealed tube; mixed m.p. with commercial C_2Cl_6 (Matheson, Coleman and Bell) 186–187.5°. Quantitative gas chromatographic analyses were made with a modified Reco Distillograph Model D-2000 (Research Specialties, Richmond, California) using the organic layers left after thiosulfate titration of the entire mixture. For C_2Cl_6 determinations a Silicone GE-SF96 (Wilkins Instrument and Research, Inc., Walnut Creek, Calif.) column packing was used; 9', 1/4" diam. tubing; column temp. 138–142°; carrier gas (He) flow: 28 ml./min.; 1-decene as internal standard. For C_2Cl_4 determinations, the column packing used was Silicone DC-11 (Research Specialties); 8', 1/4" diam. tubing; temp. 90–94°; carrier gas (He) flow: 28 ml./min.; *m*-xylene as internal standard. Peak heights were measured. The precision of the gas chromatographic method itself, estimated from chromatograms made with known amounts of C_2Cl_4 or C_2Cl_6 and internal standard, is within *ca.* 3%. Less precision (to within $\sim$ 5%) accompanied the analyses of ultrasonorated material because the organic aliquots were slightly wet, being withdrawn by syringe from an aqueous–organic system. The error in C_2Cl_4 determinations, especially for short runs, was much greater than the error in C_2Cl_6 determinations because of the significantly smaller amounts of C_2Cl_4 and correspondingly lower peak heights.

Results

Results of analyses for products from the ultrasonoration of CCl_4–H_2O and $HCCl_3$–H_2O in an inert atmosphere are summarized in Table I. Table II includes the rate data for formation of certain products from the chlorinated hydrocarbons and for peroxide production from deaerated water under the same conditions.

The absence of CCl_3COOH, or $HCCl_3$ from among the CCl_4 products is noteworthy. No chlorinated hydrocarbons other than C_2Cl_6 and C_2Cl_4 were detected although the gas chromatograms were carefully searched for their presence.

In contrast to the CCl_4 system, no CO_2, Cl_2, or any other oxidizing agent was ever found among the products from $HCCl_3$. Trace amounts of O_2 were detected as compared with the relatively large amounts formed from the CCl_4 reaction. Much less C_2Cl_6 was produced from $HCCl_3$ than from CCl_4; trace amounts of C_2Cl_4 were formed; no other chlorinated hydrocarbons were detected.

Table III shows how variation in amount of reagents affects the yield.

Discussion

Precision and Reproducibility of Results.—Throughout the history of ultrasonic reactions there has been persistent recurrence of difficulties in obtaining quantitatively reproducible results. The present investigation offers no exception. Divergence in results as great as 30% occurred more often than would be expected on a statistical basis. Such deviant data were discarded and the

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(17) The acoustical energy measurements were made by Josephine N. McFadden working under National Science Foundation Undergraduate Research Participation Grant No. EO/3/43-1427, summer, 1960.

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TABLE I

OBSERVED PRODUCTS FROM THE ULTRASONORATION OF AQUEOUS CCl_4 AND $HCCl_3$ IN AN ARGON ATMOSPHERE

Reactants	Products CO_2[a]	O_2[a]	H_2O_2[a]	CCl_3COOH[a]	$HCCl_3$[a]	Cl_2[b]	Cl^-[b]	H^+[c]	C_2Cl_4[b]	C_2Cl_6[b]
2 ml. $HCCl_3$, 20 ml. H_2O	0	trace	0	..	..	0	+	+	trace	+
2 ml. CCl_4, 20 ml. H_2O	+	+	0	0	0	+	+	+	+	+

[a] Qualitative tests on 2 hr. runs, 20°. [b] Quantitative determinations on runs from 15 min. to 3 hr.; see Table II for rates. [c] Quantitative determinations on 2 hr. runs only; in all analyses $(H^+) = (Cl^-)$.

TABLE II

OBSERVED RATES OF APPEARANCE OF PRODUCTS FROM ULTRASONORATION OF CCl_4, $HCCl_3$ AND H_2O IN AN ARGON ATMOSPHERE; 6.1 WATTS ACOUSTICAL POWER; 1 MC./SEC. FREQUENCY

Substrate	Temp., °C.	Rate	Standard error	No. of time intervals for which data were obtained	Remarks
2 ml. CCl_4, 20 ml. H_2O	20	$\frac{d(Cl)}{dt} = 9.6$ μequiv./min.	±0.45	8 (from 15–180 min.)	Total (Cl) includes (Cl^-) plus converted Cl_2. Initial non-linear rate faster than steady state linear rate established after ~40 min. at 20° and ~25 min. at 35°. Initial rate slower at 35° than at 20°.
	35	$\frac{d(Cl)}{dt} = 9.6$ μequiv./min.	...	4 (from 15–180 min.)	$(Cl)^{20°}_{40\ min.} = 7.0 \times 10^{-4}$ eq.; $(Cl)^{20°}_{180\ min.} = 20.5 \times 10^{-4}$ eq. $(Cl)^{35°}_{25\ min.} = 3.7 \times 10^{-4}$ eq.; $(Cl)^{35°}_{180\ min.} = 18.6 \times 10^{-4}$ eq.
2 ml. CCl_4, 20 ml. H_2O	20	$\frac{d(Cl_2)}{dt} = 0.5$ μequiv./min	±0.14	16 (from 15–180 min.)	Initial non-linear rate faster than steady state linear rate established after ~30 min. $(Cl_2)_{30\ min.} = 1.5 \times 10^{-4}$ eq.; $(Cl_2)_{180\ min.} = 2.2 \times 10^{-4}$ eq.
2 ml. CCl_4, 20 ml. H_2O	20	$\frac{d(C_2Cl_6)}{dt} = 4.2$ μmoles/min.	±0.25	9 (from 40–180 min.)	Initial non-linear rate slower than steady state linear rate established after ~40 min. $(C_2Cl_6)_{40\ min.} = 0.6 \times 10^{-4}$ moles; $(C_2Cl_6)_{180\ min.} = 6.5 \times 10^{-4}$ moles
2 ml. CCl_4, 20 ml. H_2O	20	$\frac{d(C_2Cl_4)}{dt} = 0.3$ μmoles/min.	...	4 (from 90–180 min.)	Concn. too low to measure before 90 min. Precision of all data low (see Experimental); actual results (av. moles): 90 min. 0.8×10^{-5}; 120 min. 1.4×10^{-5} 150 min. 2.1×10^{-5}; 180 min. 3.1×10^{-5} moles
2 ml. $HCCl_3$, 20 ml. H_2O	20	$\frac{d(Cl^-)}{dt} = 4.1$ μequiv./min.	±0.22	7 (from 15–120 min.)	Initial non-linear rate faster than steady state linear rate established after ~15 min. $(Cl^-)_{15\ min.} = 1.1 \times 10^{-4}$ eq.; $(Cl^-)_{120\ min.} = 5.4 \times 10^{-4}$ eq.
20 ml. deaerated H_2O	20	$\frac{d(H_2O_2)}{dt} = 6.6 \times 10^{-2}$ μmoles/min.	...	5 (from 10–120 min.)	H_2O_2 production started slowly, rose comparatively rapidly and tapered off to steady state linear rate after ~40 min. Early reaction faster at 35° than at 20°.
	35	$\frac{d(H_2O_2)}{dt} = 6.6 \times 10^{-2}$ μmoles/min.	...	4 (from 15–120 min.)	$(H_2O_2)^{20°}_{40\ min.} = 4.0$ μmoles; $(H_2O_2)^{20°}_{120\ min.} = 9.3$ μmoles $(H_2O_2)^{35°}_{40\ min.} = 5.0$ μmoles; $(H_2O_2)^{35°}_{120\ min.} = 10.3$ μmoles

TABLE III

EFFECTS OF VARIOUS AMOUNTS AND RATIOS OF CCl_4–H_2O ON YIELD OF TOTAL INORGANIC CHLORINE; 2 HOUR RUNS; 20°

Ml. CCl_4	Yield, equiv. Cl $\times 10^4$ 20 ml. H_2O	100 ml. H_2O
10.0	...	16.1
5.0	...	17.0
3.0	...	16.0
2.0	14.7	16.1
0.4	14.5	...
0.2	15.2	15.3

precision of the information used for calculation of rates is indicated above (see Experimental).

The causes of these large deviations lie not in the analytical procedures themselves but in some aspect of the ultrasonic procedure. At least three sources of error can be suggested. (1) Unless the coupling of the transducer to the reaction vessel is identical from run to run there will be variations in the intensity of the sound reaching the reacting medium with consequent variations in the yield. The use of Saran-bottomed vessels greatly facilitates, but does not guarantee, reproducibility in coupling. (2) A high frequency generator does not maintain absolutely constant electrical output; the acoustical output varies accordingly. Ideally the reacting system should be monitored constantly by some suitable energy detector and compensation should be made for fluctuations in sound intensity. (3) The amount of gas dissolved in the reacting liquids at the start of reaction is apparently significant. When care was taken to thermostat the water at 20° during argon saturation just prior to reaction, the analytical results (H_2O_2) were precise within 2–3%, representing the best reproducibility attained in this investigation. When, however, gas saturation was effected at the prevailing room temperature (20–27°) reproducibility was only within 6%.

Cavitation and Chemical Reaction.—All chemical reactions occurring in an ultrasonic field are governed by cavitation, which is the formation and collapse of either gaseous or vapor bubbles within the liquid.[24] Various theories have been advanced to account for the chemical activation associated with cavitation. At low sound intensities the activation has been attributed to either electrical,[25] thermal,[26] or pressure[27] phenomena which are coincident with bubble collapse. At extremely high intensities there is evidence for the importance of mechanical effects resulting from shearing action in the liquid adjacent to the resonating bubble.[9d] The initiation or acceleration of chemical reaction is most often achieved in the presence of water, the peculiar efficacy of which must reside in some unique aqueous property, or combination of properties, which allows abnormally high energy release during the cavitation process. For example, the surface tension of water is 72.75 dynes/cm. at 20° compared with approximately 25 dynes/cm. for most organic liquids. This could account for greater energy release on collapse of bubbles formed in water.

In the discussion which follows attention will first be focused on evidence which supports the idea that the cavitation bubbles are indeed the reaction sites. It will then be shown that certain rate results can be understood only by considering how the reacting system itself affects the cavitation process. Finally a mechanism accounting for the observed products will be presented.

When CCl_4 alone was ultrasonorated at an intensity of 6.1 acoustical watts, some cavitation occurred but there was no reaction. When as little as 1 ml. of H_2O was added to 100 ml. of CCl_4, reaction ensued. The total inorganic chlorine yield is not significantly sensitive to large changes in the ratio of CCl_4 to H_2O as can be seen from Table III. These results as well as the zero order[28] temperature-independent reaction rates are what would be expected if the rate-determining steps occur in the cavitation bubbles. As long as sufficient reactant is available the amount which enters the cavitation bubbles per unit of time will be constant and depend on the vapor pressure of the compound. Furthermore, if no chain reactions are involved, and if more molecules are available than energy requisite for reaction, the reaction rate will be determined only by the energy, which is, in turn determined by the amount and intensity of cavitation. The temperature independence of $[d(Cl)/dt]^{CCl_4}$ and $d(H_2O_2)/dt$ implies that the intensity of cavitation is not significantly altered over a 15° ambient temperature rise, also that the rates of primary reactions are indeed determined by the cavitation energy alone: more molecules of reactant would be expected to enter the bubbles at 35° than at 20° (v.p. in mm. Hg: H_2O, 20°, 17.5; 35°, 42.2; CCl_4, 20°, 89.2; 35°, 174). The equality of rates at the two temperatures incidentally emphasizes our poor understanding of the causes of inhibition of cavitation effected by certain volatile materials.[16,29] The very slight difference in total yield of inorganic chlorine when the amount of water is increased from 20 to 100 ml. (Table III) is consistent with the proposal that the amount and intensity of cavitation determine reaction rates, since the opportunity for effective cavitation is increased only a little, if at all, as the amount of water is increased. Even if the sound energy were sufficient to support more cavitation than occurs in 20 ml., the bubbles themselves place an upper limit on the amount of cavitation which can be produced.[29]

It is instructive to consider possible reasons for the change in some rates (Cl from CCl_4; Cl^- from $HCCl_3$; and H_2O_2 from H_2O) over the initial period of reaction (see Table II). The causes for these changes cannot be the same in the peroxide case as in the chlorine cases. Consider first the homogenous reacting medium, H_2O. Our data for H_2O_2 production reveal an initial slow rate, lasting a few minutes, followed by a faster rate which is, within 40 min., finally superseded by a slower constant reaction velocity (6.6×10^{-2} μmoles/min.). Parke and Taylor,[11] who followed this reaction during its early stages, also noted an initial increase in rate which they attributed to ultrasonic degassing; although some of the evidence concerning this point is conflicting,[11] there are indications that the gas content of a liquid can influence the efficiency of cavitation[15c] (see also Precision of Results). The final constant rate probably results from the eventual establishment of chemical equilibrium involving the decomposition of some of the peroxide formed. Such a reaction has been incorporated in the mechanism proposed for the ultrasonic reactions of water in an inert atmosphere.[12,13]

$$\mathrm{HOH} \longrightarrow \mathrm{H}\cdot + \cdot\mathrm{OH} \qquad (1)$$

$$2\,\mathrm{H}\cdot \longrightarrow \mathrm{H_2} \qquad (2)$$

$$2\,\cdot\mathrm{OH} \longrightarrow \mathrm{H_2O_2} \qquad (3) \qquad \Delta E_{\mathrm{H_2O_2}}{}^{\mathrm{dissoc.}} = +52 \text{ kcal.}^{30}$$

$$\mathrm{H}\cdot + \mathrm{H_2O_2} \longrightarrow \mathrm{H_2O} + \cdot\mathrm{OH} \qquad (4) \qquad \Delta H = -68 \text{ kcal.}^{30}$$

$$\mathrm{HO}\cdot + \mathrm{H_2} \longrightarrow \mathrm{H_2O} + \mathrm{H}\cdot \qquad (5)$$

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[24] (a) A. E. Crawford, "Ultrasonic Engineering," Butterworths Scientific Publications, London, Eng., 1955, Chap. 2; (b) ref. 29, pp. 225–234.

[25] (a) E. N. Harvey, *J. Am. Chem. Soc.*, **61**, 2392 (1939); (b) J. Frenkel, *Acta Physicochim. U.R.S.S.*, **12**, 317 (1940); (c) N. Miller, *Trans. Faraday Soc.*, **46**, 546 (1950).

[26] M. E. Fitzgerald, V. Griffing and J. Sullivan, *J. Chem. Phys.*, **25**, 926 (1956).

[27] M. Kornfeld and L. Suvorov, *J. Appl. Phys.*, **15**, 495 (1944).

[28] It should be pointed out that although the constancy of experimental rates is cited as evidence of the dominating role played by cavitation, the linearity of the total chlorine production from CCl_4 is perhaps fortuitous since, as is suggested in the text, there are evidently several reactions leading to Cl^- from CCl_4, some of which are independent of cavitation. As discussed under Mechanism the rates of appearance of Cl_2 and C_2Cl_6, from CCl_4 are each the resultant of a rate of formation and a rate of consumption.

[29] T. F. Hueter and R. H. Bolt, "Sonics," John Wiley and Sons, Inc., New York, N. Y., 1955, Chap. 6.

[30] Bond dissociation energies and the resonance energy of $\cdot CCl_3$ are taken from C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 48–50. ΔH values were calculated from appropriate bond dissociation energies.

The decrease in rate of the peroxide production after 40 minutes may be attributed to increased importance of reaction 4 as the H_2O_2 concentration builds up. Del Duca's isotope analyses[12] imply that the reverse of reaction 3 does not occur to any significant extent; furthermore, reaction 4 is energetically the more favorable.

A similar argument cannot be valid for the production of chloride ion from $HCCl_3$ and CCl_4 (total chlorine minus Cl_2), since there is little likelihood that the ion can get into the cavitation bubble to undergo reverse reaction even if such reaction were feasible. In the heterogeneous systems the decrease in reaction rate may be associated with the slow emulsification which occurs during the first 30 to 40 minutes of ultrasonoration. It is known that the cavitation threshold and degree of cavitation depend on many characteristics of the supporting liquid.[29] The emulsified liquid may not support cavitation, and therefore reaction, as effectively as the simple two-phase system. Added to this effect, in CCl_4, is the fact that CO_2 is a product and this gas is known to inhibit the progress of many ultrasonic reactions, including the disruption of the CCl_4 molecule.[31]

If cavitation is indeed less effective in the emulsified liquid, a possible explanation is at hand for the fact that the initial rate of total inorganic chlorine production from CCl_4 is not as fast at 35° as at 20°.[32] Emulsification occurs more quickly at the higher temperatures[33] (interfacial tension, CCl_4–H_2O, 45.05 dynes/cm. at 20°; 43.55 dynes/cm. at 35°).[34] The slower constant rate sets in sooner with consequent lower yields of total inorganic chlorine at the higher than the lower temperature.

Reaction Mechanisms.—Cavitation evidently provides the energy which promotes chemical transformations. Whether the nature of this energy is thermal, electrical, or otherwise, there is good evidence that in certain cases it causes homolytic bond scission.[11–13] The resulting free radicals may then react within the cavitation bubble or outside of it. The reactions of CCl_4 and $HCCl_3$ in aqueous suspension in an inert atmosphere can be interpreted on the basis of a free radical mechanism.

Energy requirements suggest that if H_2O can undergo homolytic dissociation,[12,13] CCl_4 and $HCCl_3$ molecules, which must also be present in the cavitation bubbles, should likewise experience primary cleavage

ΔE^{30}, kcal.

$$\mathrm{HOH} \longrightarrow \mathrm{HO}\cdot + \cdot\mathrm{H} \qquad (1) \qquad +120$$

$$\mathrm{CCl_4} \longrightarrow \cdot\mathrm{CCl_3} + \cdot\mathrm{Cl} \qquad (6) \qquad +\ 68$$

$$\mathrm{HCCl_3} \longrightarrow \mathrm{H}\cdot + \cdot\mathrm{CCl_3} \qquad (7) \qquad +\ 90$$

$$\mathrm{HCCl_3} \longrightarrow \cdot\mathrm{Cl} + \cdot\mathrm{CHCl_2} \qquad (8) \qquad \ldots$$

Because of the high resonance energy of $\cdot CCl_3$ (12 kcal.[30]), reaction 7 is expected to occur to some extent, despite the fact that in general C–H bonds are stronger than C–Cl bonds.

Once the radicals are freed their subsequent fate will depend on their concentrations and on energy considerations. Consider these displacement reactions

CCl_4 Kcal.[30,35]

$$\mathrm{H}\cdot + \mathrm{CCl_4} \longrightarrow \mathrm{HCl} + \cdot\mathrm{CCl_3} \qquad (9) \qquad \Delta H = -34,\ E_a \sim 3.3$$

$$\cdot\mathrm{Cl} + \mathrm{CCl_4} \longrightarrow \mathrm{Cl_2} + \cdot\mathrm{CCl_3} \qquad (10) \qquad \Delta H = +10,\ E_a \sim +12$$

$$\mathrm{HO}\cdot + \mathrm{CCl_4} \longrightarrow \mathrm{HOCl} + \cdot\mathrm{CCl_3} \qquad (11) \qquad \Delta H = +8$$

$HCCl_3$

$$\mathrm{H}\cdot + \mathrm{HCCl_3} \longrightarrow \mathrm{H_2} + \cdot\mathrm{CCl_3} \qquad (12) \qquad \Delta H = -14.2,\ E_a\ \text{low}^{36}$$

$$\mathrm{H}\cdot + \mathrm{HCCl_3} \longrightarrow \mathrm{HCl} + \cdot\mathrm{CHCl_2} \qquad (13) \qquad E_a \sim 4.3$$

$$\cdot\mathrm{Cl} + \mathrm{HCCl_3} \longrightarrow \mathrm{HCl} + \cdot\mathrm{CCl_3} \qquad (14) \qquad \Delta H = -13,\ E_a \sim 4.3$$

$$\mathrm{HO}\cdot + \mathrm{HCCl_3} \longrightarrow \mathrm{HOH} + \cdot\mathrm{CCl_3} \qquad (15) \qquad \Delta H = -30$$

The concentration of molecules at the reaction site is probably greater than the concentration of primary free radicals, leading to the expectation that radical coupling will compete successfully only when high activation energies are associated with the displacement reactions available to a given radical. Atomic hydrogen could react according to the highly probable reactions 9, in CCl_4, or 12 and 13, in $HCCl_3$; there is evidence that 12 is preferred over 13.[37] The low activation energy of reaction 14 would suggest that any atomic chlorine formed by reaction 8 would be consumed by displacement to the exclusion of chlorine–chlorine coupling, thus accounting for the absence of Cl_2 among the products from the $HCCl_3$ reaction. The less favorable activation energy for a similar reaction between $\cdot Cl$ and CCl_4, equation 10, would allow the coupling of chlorine atoms to contribute substantially to the production of the observed Cl_2 from CCl_4. By the same argument, hydroxyl radical coupling could compete successfully with the endothermic displacement by $\cdot OH$ on CCl_4, reaction 11; but the analogous reaction 15, which is exothermic, would be expected to be more likely than hydroxyl coupling in $HCCl_3$.

This brings us to the conclusion that H_2O_2 could be formed from the CCl_4 system and not to any marked extent from the $HCCl_3$ system. Its presence was observed in neither case; however, the fact that it was not found among the products does not preclude its formation. Any H_2O_2 produced in the CCl_4-H_2O mixtures would be consumed

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(31) V. Griffing, *J. Chem. Phys.*, **18**, 997 (1950).

(32) It has been suggested that the lower yields of total chlorine at the higher temperature are more apparent than real because of the lower solubility of Cl_2 at the higher temperature and consequent losses of Cl_2 into the gas phase. This is considered unlikely for two reasons: (1) in the analytical procedure NH_4OH was introduced directly into the reaction vessel through the inlet tube and the Cl_2 was fixed before the top was removed (see Experimental); (2) the solubility of Cl_2 in water alone is approximately 0.1 g./20 g. H_2O at 35° (interpolated from Handbook values); the amount of Cl_2 produced during an ultrasonic reaction is less than this by more than a power of ten. In addition, CCl_4, a very good solvent for Cl_2, is present.

(33) See, however, C. Bondy and K. Sollner, *Trans. Faraday Soc.*, **32**, 556, 616 (1936). These authors state several times that high temperature is disadvantageous to ultrasonic emulsification. No experimental temperatures, frequencies or sound intensities are mentioned in their articles, thus making it difficult to compare their results with those recorded here.

(34) W. D. Harkins and Y. C. Cheng, *J. Am. Chem. Soc.*, **43**, 35 (1921).

(35) Activation energies are taken from E. W. R. Steacie, "Atomic and Free Radical Reactions," 2nd ed., Reinhold Publ. Corp., New York, N. Y., 1954, Ch. X.

(36) E. Cremer, J. Curry and M. Polanyi, *Z. physik. Chem.*, **B23**, 445 (1933).

(37) (a) M. S. Kharasch, E. V. Jensen and W. H. Urry, *J. Am. Chem. Soc.*, **69**, 1100 (1947); (b) M. J. Boeseken and H. Gelissen, *Rec. trav. chim.*, **43**, 869 (1924); (c) A. F. A. Reijhart, *ibid.*, **46**, 72 (1927); (d) D. F. DeTar and D. V. Wells, *J. Am. Chem. Soc.*, **82**, 5839 (1960).

according to reaction 16 which can also account for both the nearly steady concentration of Cl_2, after the first half hour of reaction, and the appearance of O_2

$$H_2O_2 + Cl_2 \longrightarrow HCl + O_2 \qquad (16)$$

In order to explain the experimental data it is necessary to assume that reaction 16 is fast and that, in the early period of reaction, the Cl_2 is made at a faster rate than is peroxide; as reaction time increases, the two rates become approximately equal, the Cl_2 rate being very slightly faster than the peroxide rate. Traces of O_2 found among the products from $HCCl_3$ could result from HCl catalyzed[38] decomposition of peroxide formed in trace amounts by ·OH coupling.

Coupling of the trichloromethyl radicals leads to C_2Cl_6

$$2{\cdot}CCl_3 \longrightarrow C_2Cl_6. \qquad (17)$$

This reaction has been postulated many times as a source of C_2Cl_6 in a variety of systems.[39] In $HCCl_3$, coupling could take place between $\cdot CHCl_2$, produced by reaction 8 or 13, and ·H; further attack by hydrogen atoms on CH_2Cl_2 would lead to the ultimate production of CH_3Cl[40] which could not have been detected by our analytical methods.

Tetrachloromethylene can be formed from hexachloroethane *via* the pentachloroethyl radical, which could originate either from reaction 18 or 19.

$$C_2Cl_6 \longrightarrow \cdot C_2Cl_5 + \cdot Cl \qquad (18)$$

$$\begin{array}{lcll} & & & E^{30}_{dissoc.}, \text{ kcal.} \\ & \cdot OH \not\longrightarrow & HOCl & 60 \text{ for } HOCl \\ C_2Cl_6 + & \cdot H \longrightarrow & \cdot C_2Cl_5 + HCl \quad (19) & 130 \text{ for } HCl \\ & \cdot Cl \not\longrightarrow & Cl_2 & 58 \text{ for } Cl_2 \end{array}$$

Disproportionation of the $\cdot C_2Cl_5$ would lead to C_2Cl_4

$$2{\cdot}C_2Cl_5 \longrightarrow C_2Cl_4 + C_2Cl_6 \qquad (20)$$

If chlorine abstraction occurs and follows the same pattern in both $HCCl_3$ and CCl_4, ·H is the correct choice for the abstractor as indicated in equation 19; bond dissociation energies support this alternative.

It has been suggested that intermediate $\cdot C_2Cl_5$ can react with O_2 to form CCl_3COCl and $COCl_2$ in the chlorine-sensitized photoöxidation of HC_2Cl_5[41] and C_2Cl_4[42] in non-aqueous media. Oxygen–radical interaction may likewise be invoked here to account for the production of CO_2 from the CCl_4 system and its absence from the $HCCl_3$ system, which is essentially devoid of oxygen

$$\begin{array}{c} \cdot C_2Cl_5 + O_2 \rightleftarrows 2COCl_2 + \cdot Cl \qquad (21) \\ \Big\downarrow H_2O \\ 2CO_2 + 2HCl \end{array}$$

Reaction between $\cdot CCl_3$ and O_2 could also lead to CO_2.[35] The alternate oxidation of the pentachloroethyl radical to form CCl_3COCl does not occur in the ultrasonic reaction: we demonstrated repeatedly that neither CCl_3COOH nor $HCCl_3$, the expected decomposition product thereof, was present among the CCl_4 products. In order to test the possibility that CO_2 arose from intermediate phosgene, ethanol, known to destroy $COCl_2$, was added to the CCl_4 (about 1% solution) before ultrasonoration. The character of the reaction changed and a semi-solid yellow oil was produced which has not yet been further characterized. Contrary to expectation, CO_2 was still a constituent of the gas above the reacted mixture. It should be noted in this connection that although CO_2 was not an observed product from $HCCl_3$, in good accordance with the above scheme, the evidence must be considered in the light of the fact that the $HCCl_3$ used was stabilized with up to 0.75% alcohol.

If the above proposals approximate the correct mechanism, the rate of appearance of C_2Cl_6 (and possibly also C_2Cl_4[42]) is the resultant of two processes. Consumption as well as production of C_2Cl_6 might well be expected to be zero order, establishing an over-all linear rate once the concentration of C_2Cl_6 reached a sufficiently high value. The low vapor pressure of C_2Cl_6 (m.p. 187° in a sealed tube; b.p. 184°) may restrict the amount of this substance in the bubbles to such a low level that, for reaction 18, available energy is not the sole rate-determining factor.

The experimental results obtained in this study support the hypothesis that the ultrasonic reactions of CCl_4 and $HCCl_3$, in aqueous suspension, proceed by primary free radical reactions, followed by the interaction of some of the original products with each other.

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(38) A. Mohammad and H. A. Liebhafsky, *J. Am. Chem. Soc.*, **56**, 1680 (1934).

(39) (a) E. C. Kooyman and E. Farenhorst, *Rec. trav. chim.*, **70**, 867 (1951); (b) Von K. Pfordte, *J. prakt. Chem.*, [4] **5**, 196 (1957); (c) J. W. Schulte, *J. Am. Chem. Soc.*, **79**, 4643 (1957); (d) E. I. Heiba and L. C. Anderson, *ibid.*, **79**, 4940 (1957).

(40) H. Fromherz and H. Schneller, *Z. physik. Chem.*, **B20**, 158 (1933).

(41) H. J. Schumacher and W. Thurauf, *ibid.*, **A189**, 183 (1941).

(42) Ref. 30, p. 448.