Modeling of Sonochemical Decomposition of CCl₄ in Aqueous Solutions

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In the context of removal of organic pollutants from
wastewater, sonolysis of CCl₄ dissolved in water has been
widely investigated. These investigations are either
completely experimental or correlate data empirically. In
this work, a quantitative model is developed to predict
the rate of sonolysis of aqueous CCl₄. The model considers
the isothermal growth and partially adiabatic collapse
of cavitation bubbles containing gas and vapor leading to
conditions of high temperatures and pressures in them,
attainment of thermodynamic equilibrium at the end of col-
lapse, release of bubble contents into the liquid pool, and
reactions in the well-mixed pool. The model successfully
predicts the extent of degradation of dissolved CCl₄, and
the influence of various parameters such as initial concen-
tration of CCl₄, temperature, and nature of gas atmosphere
above the liquid. In particular, it predicts the results of
Hua and Hoffmann (*Environ. Sci. Technol.* **1996**, *30*, 864−
871), who found that degradation is first order with CCl₄
and that Argon as well as Ar−O₃ atmospheres give the same
results. The framework of the model is capable of
quantitatively describing the degradation of many dissolved
organics by considering all the involved species.

Introduction

Power ultrasound has been found to cause a number of
chemical effects (*1−5*). Recently, its use for decomposing
dissolved organic contaminants in water has been reported.
Carbon tetrachloride is one of the organic contaminants in
water which is difficult to degrade. Hence, a number of
reports have appeared in the literature on its sonolysis (*5, 6,
9−22*). These reports have followed the kinetics of decom-
position by monitoring CCl₄ concentration or pH or the
chloride ion concentration. In the present investigation, we
have studied its kinetics by monitoring I₂ formation from KI
solution when the latter is initially saturated with CCl₄.
Though a number of experimental measurements are now
available, there is no predictive method available to calculate
the decomposition rates based on the physics of the
phenomena involved. Only empirical methods (*9, 10*) have
been proposed. The objective of the present work is to
propose a predictive model based on the physics of the
phenomena involved and verify it against the experimental
results obtained during the present investigation as well those
already available in the literature.

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Experimental Section

Reagents. Analytical reagent grade carbon tetrachloride and
potassium iodide were used for experiments. Excess carbon
tetrachloride was added to double-distilled water, and the
mixture was mechanically agitated for 6 h in order to saturate
water with CCl₄. The resulting dispersion was then allowed
to stand overnight in a separating funnel. The supernatant
solution was assumed to contain 800 ppm CCl₄ (5.2×10^{-3}
M), which is its reported solubility in water (at 34 °C, the
temperature of experimentation) and was used to prepare
1 M KI solution.

Sonicator. A powered ultrasonic processor (Vibronics)
was used in the present work. The processor delivers the
sound energy to the reaction medium through a horn tip
with a radiating flat circular surface of 0.027 m diameter.
Power to the sonicator was supplied through a voltage
stabilizer (Microline) to offset any fluctuations in the supply.
The processor was operated at 260 mA current rating and
240 V. The frequency of the sound generated was 25 kHz.
The pressure amplitude of the sound waves was measured
using the calorimetric technique. When the liquid is soni-
cated, the energy is dissipated in the liquid and its temper-
ature rises. By measuring the rate of rise in temperature of
the liquid, the pressure amplitude of sound waves is
calculated. The details are discussed under the title pressure
amplitude of sound field.

Experimental Procedure. A glass beaker of 50 cm³
capacity was used as the reactor, which was in turn placed
inside a Perspex box through which water at room temper-
ature was circulated. The reaction mixture (10 cm³) consist-
ing of 1 M KI solution saturated with CCl₄ was added to the
reactor. The horn of the sonicator was immersed to a
constant depth in the reaction medium inside the glass
beaker. Preliminary experiments showed that, on sonication,
the solution temperature rose from room temperature (22
°C) to 34 °C within 2 min of sonication and stabilized at that
temperature. To avoid any effects of this initial spurt in
temperature, all experiments were conducted by starting with
the solution already heated to 34 °C. The temperature
remained at this level throughout the time of irradiation when
water at room temperature (22 °C) was circulated continu-
ously through the outer Perspex chamber. The sonication
of aqueous KI (1 M) solution saturated with CCl₄ was
conducted in air atmosphere. All the solutions were soni-
cated for different times (2, 5, 8, 10, 15, and 20 min), to
measure the kinetics of the reaction. A standard iodine
solution was diluted with 1 M KI solution to prepare iodine
solutions of different concentrations. These solutions were
used to prepare a calibration chart of concentration of iodine
versus absorbance measured at 354 nm in a UV spectro-
photometer (UV-2100, SHIMADZU), with 1 M KI solution as
the blank. The iodine liberated due to sonication was
determined by monitoring the absorbance at 354 nm.
Experiments were conducted under similar conditions, but
without sonication to study the rate of any loss of CCl₄ by
evaporation. In these, the concentration of CCl₄ was
monitored as a function of time by measuring the absorbance
by the liquid at 210 nm.

Development of Model

The sonochemical effects are the manifestation of cavitation,
in which bubbles of vapor cum gas expand and collapse
adiabatically yielding high temperatures and pressures (*23*).
Under these conditions, the contents of the bubble decom-
pose yielding reactive intermediates. These enter the liquid

phase and undergo reactions there (*24*), giving rise to the various observed effects.

Quantitative Description of the Model. The model essentially involves three main components: (i) the determination of the extreme conditions of temperature and pressure obtained in the bubble at the end of collapse, (ii) the composition of the bubble under the extreme conditions, and (iii) the reactions involving the released components and the liquid-phase reactants.

Determination of the Extreme Conditions. The extreme temperatures and pressures were obtained following Naidu et al. (*24*). The bubble dynamics equation, the condition for transition from isothermal to adiabatic process, and determination of the point of collapse were the same as used by them. Hence, only the equations which need modification are discussed here. As the mass exchange of CCl_4 is very slow, we treat CCl_4 as gas. The internal pressure P_i is therefore given by $P_i = (P_{g0} + P^0_{CCl_4})(R_0/R)^3 + P^s_w$ for the *isothermal portion* and $P_i = 2P^s_w(R_2/R)^{3\gamma}$ for the *adiabatic portion*. The initial conditions for the bubble dynamics equations are $\tau = 0$, $R = R_0$ and $dR/d\tau = 0$. In the above, R is the radius of bubble at any time τ during an acoustic cycle, R_2 is the radius where transition from isothermal to adiabatic process occurs, P_{g0} and $P^0_{CCl_4}$ are the initial partial pressure of the gas and CCl_4 respectively, P^s_w is the saturation vapor pressure of water, γ is the ratio of specific heats, and τ is the time measured from the beginning of the acoustic cycle. The value of R_2 is obtained using Flynn's hypothesis (*24*):

$$(P_{g0} + P^0_{CCl_4})(R_0/R_2)^3 = P^s_w \qquad (1)$$

The expressions for P_{g0}, and $P^0_{CCl_4}$ are given in the next section. Bubbles grow and collapse continually, and the above dynamics refers to one such cycle. Thus the "initial" conditions for bubble dynamics continually change as reactions proceed due to sonication, bringing about changes in CCl_4 concentration. The process time is of course very much greater than the acoustic cycle time, thus justifying this kind of treatment.

Calculation of Temperature and Pressure at Collapse. The temperature T_f, the pressure P_f and the radius of the bubble R_f attained at the time of collapse, are calculated as earlier (*24*) by integrating the bubble dynamics equation with the initial conditions mentioned.

Initial Bubble Radius and Bubble Composition. The value of R_0 was determined following Naidu et al. (*24*). The concentration of CCl_4 changes with time, and its vapor pressure is obtained by using Henry's law. If P_{CCl_4} is the saturation vapor pressure of CCl_4,

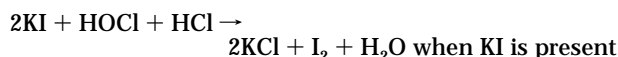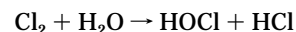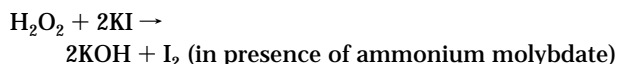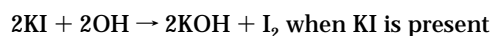$$P^0_{CCl4} = \frac{C_{CCl_4}}{C^s_{CCl4}}P^s_{CCl4}; \quad C_{CCl_4} \le C^s_{CCl4} \qquad (2)$$

where C_{CCl_4} is the concentration of CCl_4 at any instant of time (*t*), and $C^s_{CCl_4}$ is the solubility of CCl_4 in water (5.2×10^{-3} M). Equation describing the mechanical equilibrium of the bubble at the beginning of every cycle allows calculation of P_{g0}. Till the isothermal phase ends, the partial pressure of water remains constant at P^s_W (*24*), and the gas content remains constant. There is no mass exchange during the adiabatic phase. Thus, the composition during the adiabatic phase can be calculated to be

$$y_w = \frac{1}{2}; \quad y_{CCl_4} = \frac{P^0_{CCl4}}{2P^s_w}\left(\frac{R_0}{R_2}\right)^3; \quad y_g = \frac{P_{g0}}{2P^s_w}\left(\frac{R_0}{R_2}\right)^3 \qquad (3)$$

Composition of Bubble at Extreme Conditions. The collapse phase of the bubble is assumed to terminate when

its wall velocity becomes equal to the velocity of sound in the liquid. At that instant, $T = T_f$, $P = P_f$, and $R = R_f$. We assume that thermodynamic chemical reaction equilibrium is established under these conditions. The equilibrium compositions were computed using the program SOLGASMIX (*28*), which uses the concept of minimization of free energy. The inputs to SOLGASMIX are the collapse temperature and pressure, C_p vs T relationship, entropy, and enthalpy (at standard conditions) of all expected species (*29*). The mole fractions of water vapor, CCl_4, and gas at $R = R_2$ were also provided as inputs. Earlier investigations have proposed many reactions which could be taking place during collapse. The species suggested by various investigators (*5, 6, 9–22*) and given as inputs to SOLGASMIX are H_2O, N_2, O_2, CCl_4, H, OH, H_2, HO_2, $H_2 O_2$, O, Cl, Cl_2, HCl, HOCl, CO, CO_2, COCl, $COCl_2$, C_2Cl_6, C_2Cl_4, N, NO, NO_2, NO_3, NOCl, O_3, CCl_3, CCl_2, C_2Cl_2, ClO, ClO_2, Cl_2O, CNCl, NO_2Cl, CH_2Cl_2, CHCl, CH_3Cl, CH_3, C_2H_6, CH_4, C_2H, C_2HCl, C_2H_4O, C_2H_2, C_2H_4, CH_2O, C_2O, C_2N, CN_2, C_2N_2, C_4N_2, C_3O_2, C, C_2, C_3, C_4, C_5, NH_3, and N_2O. Species involving only C were included based on the formation of carbon particles during the decomposition of CS_2. Species involving C and N were included since they can, in principle, form. In the case of experiments conducted under argon atmosphere, Ar was also included among the species. The basic thermodynamic data for all species were obtained from Janaf Tables (*29*). Calculations showed most species to be present in negligible quantities. Those which were not negligible are H_2O, H, OH, HO_2, H_2O_2, N_2, O_2, O, CCl_4, Cl, Cl_2, HCl, HOCl, CO, CO_2, $COCl_2$, and C_2Cl_6. The above information was used to calculate the moles of each species in a single bubble. The total release was obtained by multiplying these values by the number of bubbles being formed per unit volume per unit time.

Rate of Reaction in Liquid Phase. Although all the species formed inside the bubble are released into the liquid, the release of Cl, Cl_2, OH, HOCl, O_2, and CO_2 is of main interest because they either participate in the liquid-phase reaction or result in change of gas composition in the bubble. The liquid-phase reactions can be listed as

$$Cl + Cl \rightarrow Cl_2$$

$$2KI + 2OH \rightarrow 2KOH + I_2 \text{ when KI is present}$$

$$OH + OH \rightarrow H_2O_2$$

$$H_2O_2 + 2KI \rightarrow$$
$$2KOH + I_2 \text{ (in presence of ammonium molybdate)}$$

$$Cl_2 + H_2O \rightarrow HOCl + HCl$$

$$2KI + HOCl + HCl \rightarrow$$
$$2KCl + I_2 + H_2O \text{ when KI is present}$$

$$2KI + HOCl \rightarrow KCl + KOH + I_2 \text{ when KI is present}$$

$$COCl_2 + H_2O \rightarrow CO_2 + 2HCl$$
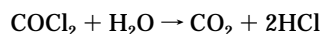
Our interest is to predict the rate of Cl^-, H^+, and I_2 formation in the liquid. Each mole of Cl_2 and HOCl yields 1 mol of I_2, respectively. However, only half of OH goes toward the formation of I_2 (*24*). On the basis of this information, the rate of liberation of various species per unit volume may be written as

$$n_{I_2} = nn_w(0.5y^e_{Cl} + y^e_{Cl_2} + y^e_{HOCl} + 0.25y^e_{OH}) = \frac{dC_{I_2}}{dt} \qquad (4)$$

$$n_{H^+} = nn_w(y^e_{HCl} + y^e_{HOCl} + y^e_{Cl} + 2y^e_{Cl_2}) = \frac{dC_{H^+}}{dt} \quad (5)$$

$$n_{Cl^-} = nn_w(0.5y^e_{Cl} + y^e_{Cl_2} + y^e_{HCl}) = \frac{dC_{Cl^-}}{dt} \quad (6)$$

$$\frac{dC_{CCl_4}}{dt} = -\left(\frac{n}{R_gT}\right)\left(\frac{4}{3}\pi R_0^3\right)\left(\frac{C_{CCl_4}}{C^s_{CCl_4}}P^s_{CCl_4}\right) + nn_wy^e_{CCl_4} \quad (7)$$

where R_g is the universal gas constant (82.05 atm cm³/gmol K) and T is the bulk temperature (307 K in our experiment). As all the CCl₄ going into the bubble is getting decomposed completely (as shown by calculations through SOLGASMIX), the contribution of second term on the right-hand side is zero. Independent experiments showed that, in our case, there was a small but continuous loss due to evaporation into the ambient, and that this was first order with respect to CCl₄. A first-order term given by $-k_eC_{CCl_4}$ was added to the left-hand side of the above equation, where k_e is an empirical coefficient which was determined by independent experiments to be equal to -0.0126 min⁻¹. The magnitude of this term was about 9% of the loss due to reaction represented by the first term of the left-hand side of the above equation. The initial conditions for the above equations are

$$C_{I_2} = 0; \ C_{H^+} = 10^{-pH}; \ C_{Cl^-} = 10^{-pH}; \ C_{CCl_4} = C_{CCl_4}(t=0) \quad (8)$$

The initial pH of the solution is used to calculate the initial concentration of hydrogen and chloride ions in the solution. Other species do not influence the kinetics.

Calculation Procedure. Equations 4–8 were solved by using Fehlberg Runge−Kutta method (subroutine rkf45). The solution requires, apart from physical properties, n, y^e_i, and P_a. Of these, n and P_a are evaluated from independent experiments. Bubble dynamics equation was solved with the relevant initial conditions, using the Livermore Solver (lsode solver) based on the backward difference method. The composition at collapse was determined using eq 3. By using this, T_f and P_f as inputs, SOLGASMIX program was used to predict y^e_i. The y^e_i were determined at every time interval of integration, which is of the order of 0.1 s, and were assumed to remain constant during this time interval. These results were insensitive to variations in the width of time interval around 0.1 s and are therefore converged results. The various physical properties required are the ratio of specific heats γ, saturation vapor pressures (P^s_w, $P^s_{CCl_4}$) and surface tension of aqueous solutions of KI. They were calculated as follows: the average value of γ is calculated using the mole fractions (x_i) for various species (24). The value of saturation vapor pressure was corrected for the presence of KI solute in water (30). Also surface tension of water was corrected using an empirical correlation (24) for the presence of KI solute in water.

Pressure Amplitude of Sound Field. The calorimetric technique (31) was used to measure the pressure amplitude (P_a) of sound waves. The pressure amplitude obtained at 34 °C for water was 1.33×10^5 N/m² and for water saturated with CCl₄, it was 1.26×10^5 N/m². R_0 corresponding to these pressure amplitudes used were fixed, after doing the sensitivity study indicated earlier, to be 2 and 2.5 μm, respectively. We have taken the value of R_0 to be 2.5 μm for our experiments as we have used water saturated with CCl₄. In predicting others' results, we have taken the value of R_0 to be 2 μm as the dissolved concentration of CCl₄ in their experiments was less than 20% saturation.

Number of Bubbles Collapsing per Unit Volume per Unit Time. The number of bubbles collapsing per unit time per unit volume, n, was found by the same procedure as used
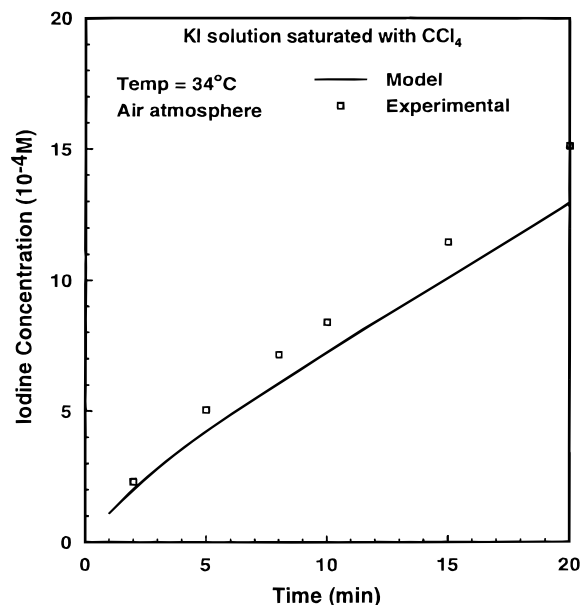

FIGURE 1. Iodine generated as a function of time during sonication of 1 M KI solution saturated with CCl₄ under air atmosphere ($n = 2.04 \times 10^{10}$ L⁻¹ s⁻¹).

earlier (24) by us. Here KI solution is sonicated in the presence of ammonium molybdate when all OH results in oxidation of KI. Knowing the OH formed per bubble through SOLGASMIX and the rate of I₂ formation per unit volume, the number of bubbles formed per unit volume per unit time was calculated. It was found to be 2.04×10^{10} L⁻¹ s⁻¹. This value has been used through out. There might be some variations in the initial rate of bubbles formation with respect to the initial concentration of dissolved CCl₄, even when the experiments are performed in the same sonicator. Since the quasisteady rate is reached very quickly with the disintegrated bubbles acting as nuclei for further cavitation, there would not be any significant variation in the steady-state value of n in a particular sonicator due to the variation in the initial dissolved concentration of CCl₄.

Verification of the Model

The model has been verified for systems where I₂ generation, change in pH, or chloride ion concentration have been used to monitor the degradation of CCl₄.

Comparison Using Rate of I₂ Generation. Figure 1 shows the change in concentration of iodine when 1 M KI solution saturated with CCl₄ was sonicated at 34 °C under air atmosphere. The rate of iodine liberation is initially high but slows down as the sonication time is increased. This is due to the depletion of dissolved CCl₄ in the solution as sonication is carried out. The model also captures this trend correctly. It is to be noted that since P_a and n have been determined from *independent* experiments, the model does not have any adjustable parameters. In view of this, the quantitative agreement between observations and theory can be considered reasonable. Table 1 shows the typical equilibrium compositions predicted by SOLGASMIX at the end of adiabatic collapse during sonication of aqueous CCl₄ solution under air atmosphere. From Table 1, it is seen that CCl₄ decomposition is almost complete in the bubble, i.e., $y^e_{CCl_4}$ was nearly equal to zero. When the concentration of dissolved CCl₄ is very low in the water, as is the case with respect to the results of other investigators (degree of saturation is less than 20%), among these products, the dominant products are CO₂, HCl, and OH. When water is initially saturated with CCl₄, the amount of chlorine and HOCl formed are higher than the hydroxyl radicals. But as the

TABLE 1: Typical Initial Equilibrium Compositions Per Mole of Water Vapor Predicted by SOLGASMIX during Sonication of Aqueous Solution of CCl_4 with Different Concentrations under Air Atmosphere

initial CCl_4 conc (ppm)	species	composition at R_2 (gmol)	equilibrium composition (gmol)
800 (saturation)	N_2	0.674 27	0.6696
	O_2	0.179 23	0.1585
	CCl_4	0.1465	5×10^{-16}
	H_2O	1.0	0.7313
	CO_2		0.1464
	OH		0.0031
	Cl		0.0138
	Cl_2		0.0186
	HCl		0.5301
	HOCl		0.0038
8	N_2	0.7888	0.7823
	O_2	0.2097	0.2016
	CCl_4	0.001 465	9.1×10^{-27}
	H_2O	1.0	0.9935
	CO_2		0.00146
	OH		0.0063
	Cl		1.97×10^{-4}
	Cl_2		1.04×10^{-6}
	HCl		5.62×10^{-3}
	HOCl		3.01×10^{-5}

degree of saturation goes down, the hydroxyl radical becomes the dominant product. It can be seen from the product distribution that the CCl_4 dissolved in water is completely transformed to products such as HCl, Cl, Cl_2, HOCl, and CO_2.

When KI solution is saturated with CCl_4, the oxidation of I^- is mainly due to chlorine. In dilute solutions of CCl_4 in water, hydroxyl radical formed are many times more than chlorine, and hence, the oxidation of I^- must be due to hydroxyl radicals. These results suggest that the major overall reactions in the bubble are

$$H_2O \rightarrow H + OH$$

$$CCl_4 + 2H_2O \rightarrow CO_2 + 4HCl$$

$$CCl_4 + H_2O \rightarrow CO + 2HCl + Cl_2$$
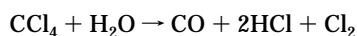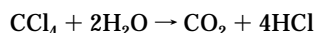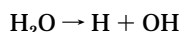
Comparison with Data Available in the Literature. There are two parameters in the model, P_a and n, whose values have to be fixed for the conditions of the observations before predictions can be made. No information regarding these is available on the systems reported in the literature. In view of this, the following procedure was adopted for fixing the values of P_a and n.

Our experiments show that CCl_4 lowers the P_a value. As most investigators have used very low CCl_4 concentration, their P_a values are likely to correspond to the values obtained with water. Hence, we have used P_a value obtained for water in our sonicator as the typical value while predicting the results of other investigators. This value may not be far removed from the actual values in their systems as the sonicators used by them are of similar type (ultrasonic probe) with comparable diameter of the horn tip and the input electrical power.

The value of n for each investigator was evaluated by using one data point, as it is specific to the sonicator used. The composition required in the evaluation was based on the vapor pressure of water at the temperature of their experiment and the initial concentration of CCl_4.

Comparison of Observation and Model Prediction for Depletion of CCl_4. Figure 2 shows the comparison between the model predictions and experimental results of Wu et al. (9) and Bhatnagar and Cheung (10). The plot shows the
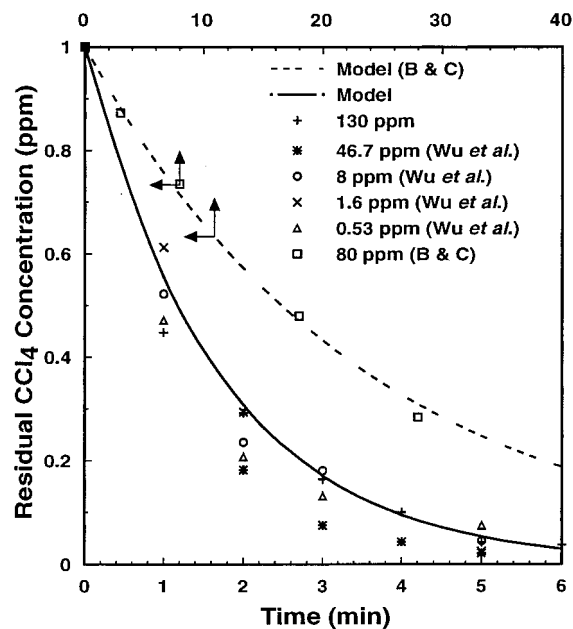

FIGURE 2. Comparison of model predictions with data of Wu et al. (9) and Bhatnagar and Cheung (10) on the variation of CCl_4 concentration with time.
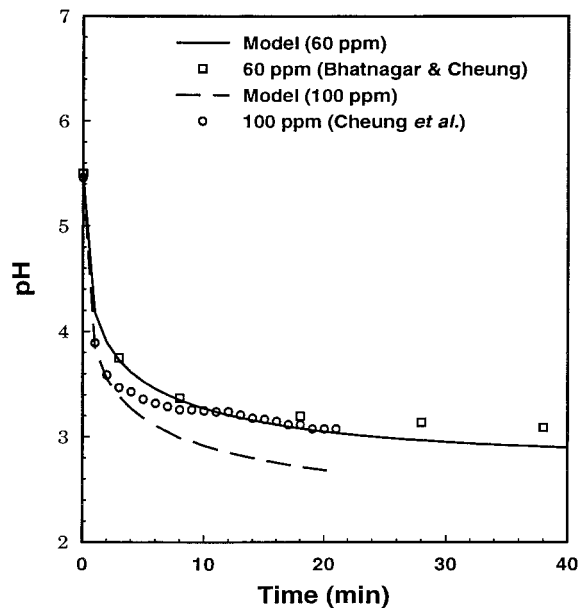

FIGURE 3. Comparison between predicted and experimental results of Bhatnagar and Cheung (10) and Cheung et al. (6) on the variation of pH with time.

depletion in CCl_4 concentration against the sonication time for different initial concentrations of CCl_4 in water. Wu et al. conducted their experiments at 25 °C in the presence of dissolved air. Bhatnagar and Cheung (10) used an initial dissolved CCl_4 concentration of 60 ppm under air atmosphere. In their experiments, the bulk temperature varied from 20 to 25 °C. The model predictions are made taking the bulk temperature to be 23 °C. The model predictions agree well with the experimental results in all cases. Under all these conditions, more than 95% depletion of CCl_4 in the liquid was achieved within 6 min of sonication, and the model predicts this well.

Comparison Using pH as Monitoring Variable. In Figure 3, the model predictions for decrease in pH are also compared with the results of Bhatnagar and Cheung (10) and Cheung et al. (6), whereas Figure 4 compares the model predictions
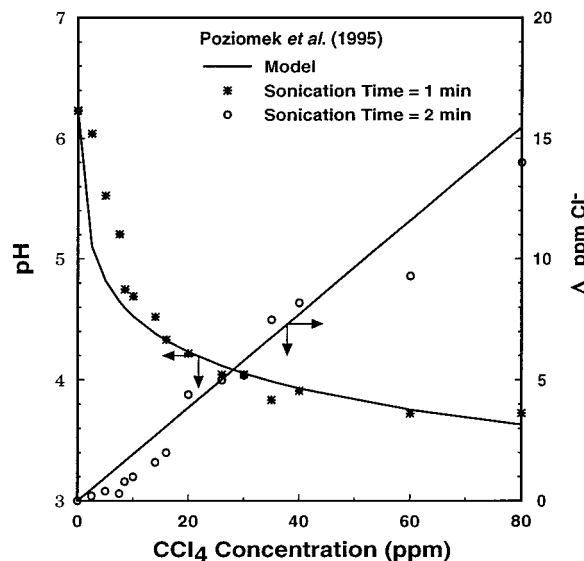
FIGURE 4. Comparison of model predictions with the experimental results of Poziomek et al. (*20*) on the variation of pH and chloride ion with the initial CCl_4 concentration at fixed times of sonication.
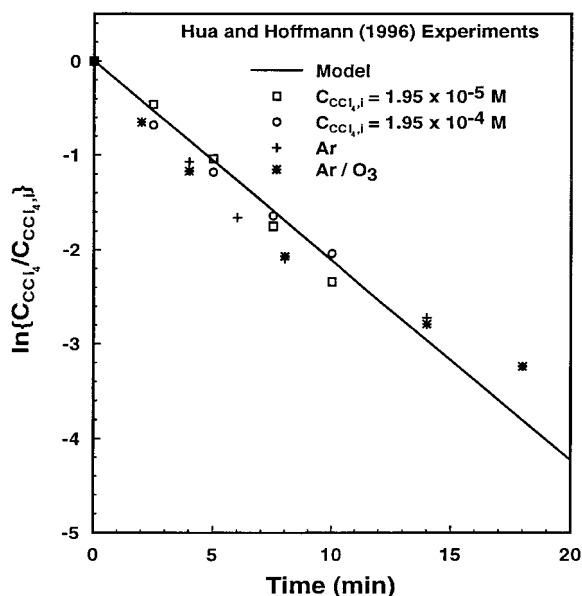

FIGURE 5. Comparison of the predictions with the experimental results of Hua and Hoffmann (*11*) on the extent of removal as well as the effect of $Ar-O_3$ composition.

with the results of Poziomek et al. (*20*). While the results of Bhatnagar and Cheung (*10*) and Cheung et al. (*6*) pertain to the variation of pH with time for a given initial concentration of CCl_4, those of Poziomek et al. (*20*) represent the pH attained after sonication of samples of different CCl_4 concentrations for one minute. The initial CCl_4 concentration, bulk temperature, and atmosphere used by Bhatnagar and Cheung (*10*) were 60 ppm, 15–20 °C, and air, while Cheung et al. (*6*) employed 100 ppm, 15–20 °C and air. The predictions made by the model using 23 °C for the experiments of Bhatnagar and Cheung (*10*) and 18 °C for those of Cheung et al. (*6*) are reasonable though there is a systematic deviation from the results of Cheung et al. at higher times. The quantitative prediction of the nonlinear behavior of the results of Poziomek et al. is excellent as is seen from Figure 4.

Comparison Using Chloride Ion as Monitoring Variable. The observations made by Poziomek et al. (*20*) on changes in the chloride ion concentration due to sonication of CCl_4 in water at 30 °C in the presence of air for a particular duration by varying the initial dissolved concentration of CCl_4 are also compared with our model predictions in Figure 4. The observations in the increase in chloride ion concentration in the range of 3–80 ppm of CCl_4 concentration in water are predicted well by the present model. As the dissolved concentration is increased, more is the CCl_4 content inside the bubble. Hence, more is the decomposition of CCl_4 leading to the formation of more HCl with increasing concentrations of CCl_4.

CCl_4 Degradation under Argon and Ozone Atmosphere. The results of Hua and Hoffmann (*11*) concerning Ar and $Ar-O_3$ mixture (44:56% v/v) have been presented in Figure 5. These authors found that the decomposition of CCl_4 is first order, and the results for Ar as well as $Ar-O_3$ are the same. The model predictions also show the reaction to be first order and the composition of the gas having negligible effect. Further, the rate constant calculated by the present model is also independent of CCl_4 concentration. Thus, the rate constants obtained by Hua and Hoffmann are 3.3×10^{-3} s^{-1} and 3.0×10^{-3} s^{-1} for initial CCl_4 concentrations of 1.95 $\times 10^{-4}$ M and 1.95×10^{-5} M, respectively, whereas the one calculated from the present model is 3.53×10^{-3} s^{-1} for both the concentrations. Again the model is able to explain the results quite well.

Effect of Bulk Temperature on Destruction Efficiency. Figure 6 shows the effect of steady-state bulk temperature
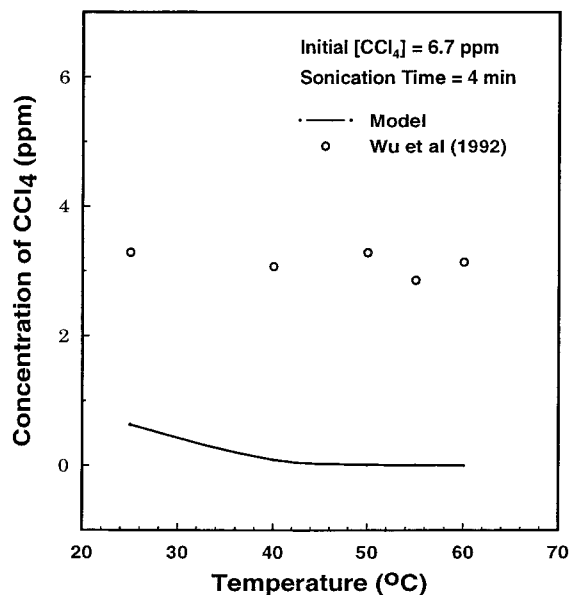

FIGURE 6. Comparison of the model with the experimental results of Wu et al. (*9*) on the effect of temperature on the reduction in CCl_4 concentration through sonication for a fixed period.

on the destruction efficiency of CCl_4 (*9*). The sonication was carried out at different temperatures between 25 and 60 °C under air atmosphere. The initial dissolved concentration of CCl_4 sonicated was 6.7 ppm in water. The experimental results and model predictions are shown for 4 min of sonication. The destruction efficiency is almost the same within this range of temperature although the destruction efficiency is slightly high at higher temperatures. This is explained by the fact that at higher temperatures cavitation becomes ineffective, but the CCl_4 composition inside the bubble increases. These two opposing effects produce a result nearly independent of temperature. The model qualitatively agrees with the experimental results but quantitative predictions show consistent deviation from the experimental data. It is difficult to explain this difference but is possibly due to the variation of *n* with temperature. Overall, the model is able to quantitatively explain not only the results of the present investigation but also those available

in the literature. Though the basic framework presented above has been tested for degradation of CCl$_4$, it is applicable to other organic systems also. However, the species involved will be different giving rise to different results of SOLGASMIX and different kinetics of reactions in the liquid phase.

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