The Site of Sonochemical Reactions

KENNETH S. SUSLICK AND DAVID A. HAMMERTON

Abstract—In order to probe the nature of the reactive site generated by acoustic cavitation, several new chemical dosimeters have been developed and the effects of physical conditions on their yields have been explored. Specifically, the effects of solution vapor pressure and dosimeter vapor pressure on sonochemical reaction rates have been examined. An excellent correlation between the log of the sonochemical rate and the solvent vapor pressure is found. This is the expected result if sonochemical reactions originate from an implosive cavitational collapse, generating a transient "hot-spot." Thus as bulk temperature is increased (and solution vapor pressure increases), the intensity of cavitational collapse, the peak temperature reached during such collapse and, consequently, the rate of sonochemical reactions all decrease. In contrast, if the solution vapor pressure is held constant and the dosimeter's vapor pressure made variable, the rate of sonochemical reaction is linear with increasing dosimeter vapor pressure and exhibits a nonzero intercept. This demonstrates for the first time that primary sonochemical reactions occur both in the vapor phase and in the liquid surrounding the cavitation event. Thus sonochemistry occurs principally to chemical species with significant vapor pressure; nonetheless, involatiles will react in the heated liquid shell surrounding the collapsing cavity or with other diffusible high-energy intermediates in the bulk solution.

INTRODUCTION

SONOCHEMISTRY, the chemical effects of high intensity ultrasound, is a topic of resurging interest for its biological [1]-[3], synthetic [4]-[10], and catalytic [11]-[15] relevance. Ultrasonic cavitation is well established as the origin of this phenomenon [16]-[18]. Transient cavitation induces the implosive collapse of gas and vapor bubbles and thus generates transient "hot-spots" with local temperatures and pressures thought to be several thousand degrees Kelvin and hundreds of atmospheres [19]-[22]. This localized hot-spot is responsible for both sonochemistry and sonoluminescence, directly for primary reactions and indirectly for secondary reactions, which occur when reactive species generated in the cavitation zone diffuse into the bulk solution and there react with other species.

Although this qualitative understanding is clear, the quantitative conditions present in the hot-spot have not yet been well defined. A variety of calculations from hydrodynamic models of cavity collapse have been made [19]-[20], but the assumptions made with respect to thermal transport, vapor concentration, etc., limit the reliability and generality of these estimates. Strikingly, the experimental determination of these conditions is extremely lim-
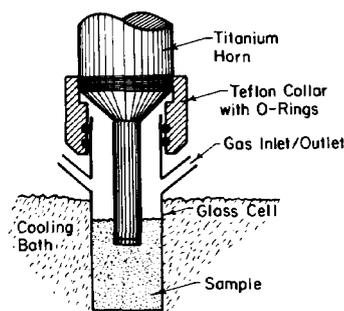
Fig. 1. Ultrasonic irradiation cell for inert atmosphere work.

ited and is based exclusively on sonoluminescence emission profiles [21]-[22]. On an even more fundamental level, the actual site of sonochemistry and sonoluminescence has not yet been established: do the primary reactions occur only in the vapor phase of the cavity or also in liquid phase surrounding the collapsing cavity? In order to probe the nature of the reaction site generated by acoustic cavitation, we have developed several new chemical dosimeters and explored the effects of physical conditions on their kinetics. This has allowed us to demonstrate definitively a correlation between solvent system vapor pressure and hot-spot temperature and to assign unambiguously both vapor and gas phase components in the associated sonochemistry.

EXPERIMENTAL SETUP

All ultrasonic irradiations were made with a collimated 20-kHz beam from a titanium amplifying horn driven by a lead zirconate titanate transducer (Heat-Systems Ultrasonics, Inc.; Model W-375P), with a total acoustic power of 24 W and acoustic intensities of 24 W/cm^2 at the horn's surface. Reactions were performed in a thermostated glass sonication cell under an Ar atmosphere, as is shown in Fig. 1 (and described in detail elsewhere [12]).

Product analyses were achieved by FT IR (Nicolet 7199 or MX-S) and UV-visible (Hitachi 100-80) spectrophotometry, as needed. Solvents were of highest available purity (spectrophotometric, gold label, or +99 percent) and used without further purification. $Fe(CO)_5$ from Alpha Ventron Chemicals was vacuum distilled immediately prior to use. $Mo(CO)_6$, $W(CO)_6$, and $Mn_2(CO)_{10}$ (from Alpha Ventron Chemicals) were +95 percent pure and used as purchased. $P(C_6H_5)_3$ (from Aldrich Chemicals) was 99 percent pure and used as purchased. $P(OC_6H_5)_3$ (from Aldrich Chemicals) was 97 percent pure and vacuum distilled before use. Vapor pressures were calculated, assuming ideal behavior, from available data [23]-[26].

RESULTS AND DISCUSSION

In order to probe the conditions generated by acoustic cavitation, we have turned to the substitution chemistry of metal carbonyls ($M_x(CO)_y$) as a useful set of chemical dosimeters for four reasons. First, metal carbonyls have explored well thermal [27] and photochemical [28] reactivities, which provide a useful background for comparison to their sonochemistry. Second, the reactivity of metal carbonyls is relatively simple; there is a weak metal–carbon bond (bond enthalpy of approximately 160 KJ/mol) and a very strong carbon–oxygen bond (bond enthalpy of approximately 1100 KJ/mol) [29]. Thus, there is little doubt as to which bond breaking is likely to occur during ultrasonic irradiation. Third, the chemical reactivity of metal carbonyls is diverse and of great importance to synthetic and catalytic organometallic chemistry [27]. Finally, the reactions of metal carbonyls are easily monitored by quantitative infrared or optical spectrophotometry.

We have reported elsewhere on the details of the sonochemistry and sonocatalysis of metal carbonyls [11]–[14], and this report focuses on their use as chemical dosimeters of acoustic cavitation. Briefly, however, we have established several unusual reactivity patterns, including the controlled multiple loss of CO leading either to the formation of metal–metal bonded clusters or to multiple ligand substitution by phosphines or phosphites and the initiation of homogeneous catalysis of olefin isomerization by normally unreactive carbonyls.

In the present studies the following reactions have been used as chemical dosimeters:

$$Fe(CO)_5 \ \longrightarrow\ xFe_3(CO)_{12} + yFe + zCO \qquad (1)$$

$$M(CO)_6 + L \ \longrightarrow\ M(CO)_5L + CO \qquad (2)$$

$$Mn_2(CO)_{10} + 2L \ \longrightarrow\ Mn_2(CO)_8L_2 + 2CO \qquad (3)$$

where L represents triphenylphosphine ($P(C_6H_5)_3$) or triphenylphosphite ($P(OC_6H_5)_3$) and M represents Mo or W. All of these reactions are kinetically well-behaved, are first order in the metal carbonyl concentration, and are zero order in the concentration of L.

During these studies, we discovered an excellent correlation between the log of the chemical dosimeter reaction rate and the vapor pressure of the solvent system [30], [31], as shown, in Fig. 2, for example. This correlation is consistent with the simple hydrodynamic models of the cavitation process. Neppiras [32], for example, derives the peak temperature generated during collapse of a *gas*-filled cavity as

$$T_{max} = \frac{T_o P_a(\gamma - 1)}{Q} \qquad (4)$$

where T_o is the ambient temperature; P_a is the acoustic pressure at initiation of collapse; γ is the ratio of specific heats; and Q is the gas pressure in the bubble at initiation of collapse. In the case of vapor-filled cavities, we may take Q very roughly equal to P_v, the vapor pressure of the solvent [33]. If we assume that the sonochemical reactions follow Arrhenius behavior ($k = A \exp(-E_a/RT_{max})$), then

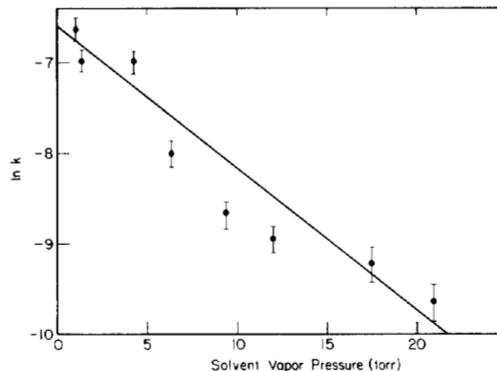Fig. 2. Natural logarithm of the observed first-order rate constant for $-d[Fe(CO)_5]/dt$ vs. solvent vapor pressure at 25°. $d[Fe(CO)_5]/dt = -k[Fe(CO)_5]$, with k in units of s^{-1}; good first-order behavior was observed for 3.5 half-lives. In order of increasing vapor pressure, data are plotted for decalin, decane, nonane, 0.22 mole fraction octane in nonane, 0.52 mole fraction octane in nonane, octane, 0.11 mole fraction heptane in octane, and 0.22 mole fraction heptane in octane.
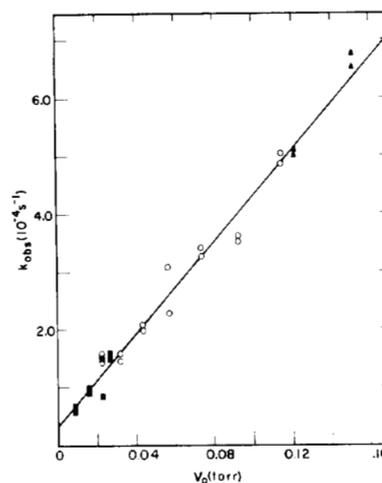

Fig. 3. Observed first-order rate constant for $-d[Fe(CO)_5]/dt$ vs. vapor pressure of $Fe(CO)_5$. Total vapor pressure of solvent system is constant at 5.0 torr. ▲ denotes the heptane/nonane mixtures, $-3°C$ to $14°C$; ○ denotes the octane/decane mixtures, $12°C$ to $39°C$; and ■ denotes the nonane/dodecane mixtures, $39°C$ to $43°C$.

$$\ln k = \ln A - \frac{E_a}{RT_o P_a(\gamma - 1)} P_v \qquad (5)$$

which has the form of the observed correlation in Fig. 2. This should be taken as only a *rough* approximation since it neglects the effects of both the thermal conductivity and the condensation of the vapor during cavitational collapse.

If one fixes the overall vapor pressure of the system by using appropriate solvent mixtures and fixes the overall dosimeter concentration in the solution, but changes the dosimeter's vapor pressure by altering the ambient temperature, one can gain information as to the actual site of the sonochemical reactions. As shown in Figs. 3–5 and presented in Table I, the dosimeter reaction rates k_{obs} increase linearly with increasing dosimeter vapor pressure V_P and have a nonzero intercept (similar results were also observed with $Mn_2(CO)_{10}$). The linear dependence on the dosimeter's vapor pressure represents the sonochemistry occurring in the vapor phase of the cavitation event: as the dosimeter vapor pressure increases, its concentration within the cavity increases, and hence its total observed
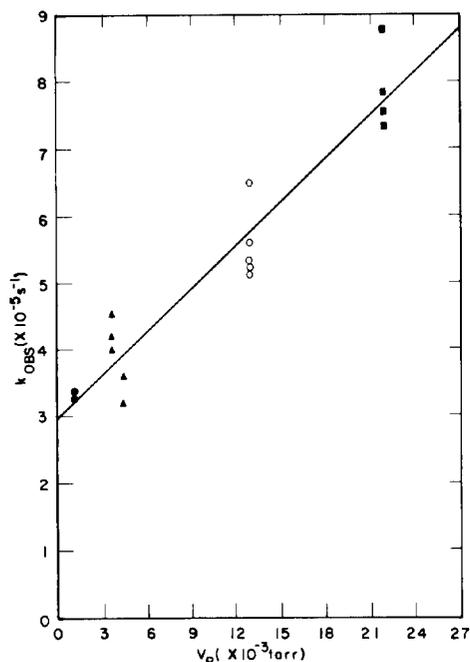
Fig. 4. Observed first-order rate constants for $-d[Mo(CO)_6]/dt$ vs. vapor pressure of $Mo(CO)_6$. The total vapor pressure of the solvent system is constant at 5.0 torr. ▲ are the octane/decane mixtures, 14°–16.5°C; ○ is the nonane/decane mixture, 35°C; and ● is the heptane/decane mixture -3.2°C; and ■ is the nonane/dodecane mixture 43°C.
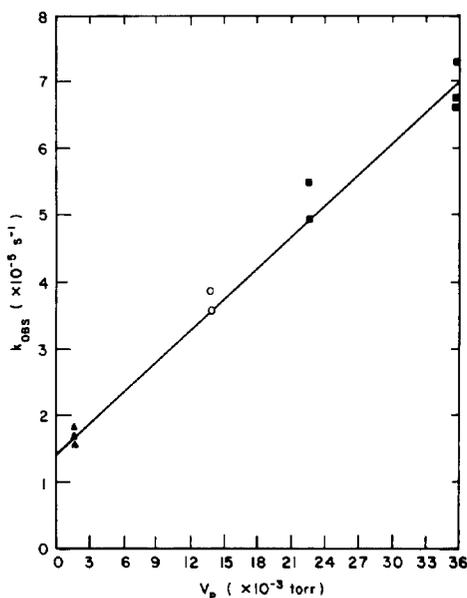

Fig. 5. Observed first-order rate constants for $-d[W(CO)_6]/dt$ vs. vapor pressure of $W(CO)_6$. The total vapor pressure of the solvent system is constant at 5.0 torr. ▲ denotes the octane/decane mixture 28°C; ○ denotes the nonane/decane mixtures 41°C; and ■ denotes the decane/dodecane mixture 53–71°C.

rate of reaction increases. The nonzero intercept, however, indicates that there is a second component to the observed sonochemistry, one that is vapor pressure independent. This must be due to reactions occurring in the *liquid phase* rather than in the vapor phase. Presumably this second reaction site is a thin liquid shell surrounding the cavity which is heated during the acoustic collapse, as shown schematically in Fig. 6.

We can use this model to generate a semi-quantitative

TABLE I
VAPOR AND LIQUID PHASE REACTION ZONE RATE COEFFICIENTS

Dosimeter	$k_v(\text{s}^{-1}\,\text{bar}^{-1})^1$	$k_l(\text{s}^{-1}\,\text{M}^{-1})$	V_{vmax}/V_{lo}
$Fe(CO)_5$	2.96(5)	$3.35(48) \times 10^{-3}$	2.2×10^4
$Mo(CO)_6$	1.63(14)	$2.97(25) \times 10^{-3}$	1.4×10^4
$W(CO)_6$	1.17(6)	$1.37(18) \times 10^{-3}$	2.1×10^4

^1k_v is the vapor phase reaction rate coefficient (taken from the slopes of the lines fit to data in Figs. 3, 4, and 5); k_l is the liquid phase reaction rate coefficient (taken from the intercepts of the data in Figs. 3, 4, and 5); and V_{vmax}/V_{lo} is (maximum cavity volume)/(liquid shell volume) just prior to collapse. The standard deviation of last digit is given in parenthesis.
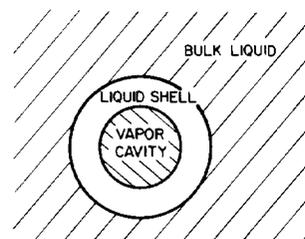

Fig. 6. Sites of sonochemical reactivity.

estimate of the relative sizes of these two reaction sites. For the moment, let us assume that all dosimeter molecules found within either the vapor or liquid phase reaction zones react during the implosive collapse of the cavities. The relative sizes of the two reaction sites are easily calculated simply by converting units of vapor pressure to molarity (1 bar $= 4.019 \times 10^{-2}$ M at 300°K) for k_v, the vapor phase reaction rate constant (taken from the slopes of the lines fit to Figs. 3–5), and dividing by k_l, the liquid phase reaction constant (taken from the intercepts of the same data), as given in Table I. This ratio (V_{vmax}/V_{lo}) represents the relative effective reaction volumes of the cavity at maximum expansion just prior to collapse versus the liquid phase volume. If $R_{lo} \ll R_{max}$

$$\frac{R_{max}}{R_{lo}} = \frac{3V_{vmax}}{V_{lo}} \qquad (6)$$

where R_{max} is the radius of the cavity immediately before the collapse; R_{lo} is the liquid shell thickness; V_{vmax} is the cavity volume; and V_{lo} is the liquid shell volume, all immediately prior to collapse. From Table I, we see that V_{vmax}/V_{lo} is approximately 2×10^4.

If we make estimates of the maximum cavity radius (R_{max}) and its minimum radius after collapse (R_{min}), then the thickness of the heated liquid shell can be calculated. The following equation yields the approximate maximum cavity radius [34]:

$$R_{max} = (4/3\omega)(2/3)^{1/3}\,(2P_o/\rho)^{1/2}\,(P_A/P_o)^{5/6} \qquad (7)$$

where ω is radial frequency $= 1.257 \times 10^5\,\text{s}^{-1}$, ρ is density $= 7.2 \times 10^2\,\text{kg/m}^3$, and P_A/P_o is ambient pressure/acoustic pressure $= 6.65$ under our experimental conditions. Thus R_{max} is approximately 6.5×10^{-4} m and the thickness of the liquid shell before collapse R_{lo} is approximately 10^{-8} m. Estimates of the minimum cavity size after collapse are rougher, since ideal behavior is lost during collapse. Nonetheless, one may expect [34], [35]

R_{max}/R_{min} to be approximately five, which implies the thickness of the liquid shell at maximum collapse is $25R_{lo}$, or about 250 nm. This corresponds to a reactive liquid layer of about 500 molecules thick which is in keeping with one's intuition for thermal dissipation. Given the macroscopic observed rates and the calculated reactive zone volumes, we can even estimate the density of cavitation events in our sample (N_{cav}):

$$N_{cav} = \frac{k_l C_l}{V_l} \sim 4 \times 10^5 \text{ s}^{-1} L^{-1} \qquad (8)$$

where k_l is the liquid phase reaction rate constant ($\sim 3 \times 10^{-3} \text{ s}^{-1} \text{ M}^{-1}$ in Table I); C_l is the concentration of dosimeter in solution (10^{-2} M); and V_l is the liquid shell volume ($\sim 7 \times 10^{-11}$ L as above).

These calculations have assumed that *all* dosimeter molecules in either reaction zone react during the cavitation event. This is equivalent to an assumption of infinite temperature in the hot-spot. While the temperatures are quite high (several thousand degrees Kelvin), this is clearly a naive assumption. In fact, the differences in k_l, k_v, and V_{vmax}/V_{lo} among the three dosimeters are due to the non-infinite temperature of the hot-spot. Given independently determined activation parameters for these reactions, the differing values of k_l and k_v may be used as "chemical thermometers" and calibrate the effective temperature at which reactions occur during cavitational collapse. Further work on this problem gives us estimated temperatures of $5200°$ K and $\sim 1900°$ K for the vapor and liquid phase reaction zones, respectively [35].

CONCLUSION

Thus we have seen that acoustic cavitation generates sonochemistry both in *vapor* and in *liquid* phases. From our experimental data one can calculate that the relative volumes of the vapor cavity and reactive liquid shell are roughly 2×10^4 to 1 before collapse. Given estimates of the cavity sizes, under these conditions the liquid shell reaction zone has a thickness of about 250 nm after collapse.

ACKNOWLEDGMENT

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Kenneth S. Suslick received the B.S. degree from the California Institute of Technology, Pasadena, CA, in 1974 and the Ph.D. in physical chemistry from Stanford University, Stanford, CA, in 1978.

He then moved to the University of Illinois at Urbana-Champaign as an Assistant Professor in the School of Chemical Sciences and was promoted to Associate Professor in 1984.

Dr. Suslick is a Sloan Foundation Research Fellow and recipient of a National Institutes of Health Research Career Development Award.

David A. Hammerton was born in Kankakee, Illinois on October 6, 1948. He received the B.A. degree in Music from the University of Illinois, Urbana, IL, in 1975.

He studied chemistry at Southern Connecticut State University in New Haven, CT, and he is currently pursuing a Ph.D. degree in Inorganic Chemistry at the University of Illinois, Urbana.

Mr. Hammerton is a member of the American Chemical Society.