

Alkane Sonochemistry

Kenneth S. Suslick,* John J. Gawlenowski, Paul F. Schubert, and Hau H. Wang

School of Chemical Sciences, University of Illinois at Urbana—Champaign, Urbana, Illinois 61801 (Received: April 26, 1983)

The chemical effects of high-intensity ultrasound on alkane solutions are reported. Primary products are H₂, CH₄, C₂H₂, and smaller 1-alkenes. Strong similarities to high-temperature (>1200 °C) alkane pyrolysis are observed and a radical chain mechanism is proposed. The principal sonochemical process appears to be C–C bond cleavage with secondary abstractions and rearrangements. In order to probe the factors which affect sonochemical yields, we have used two very different chemical dosimeters in alkane solutions: radical trapping by diphenylpicrylhydrazyl and decomposition of Fe(CO)₅. In both cases, good correlation is found between the log of the sonochemical rate and the solvent vapor pressure. This result is justifiable in terms of the cavitation "hot-spot" explanation of sonochemistry. Thus, decreasing solvent vapor pressure increases the intensity of cavitation collapse, the peak temperature reached during such collapse, and, consequently, the rates of sonochemical reactions.

Introduction

The chemical effects of high-intensity ultrasound have been extensively studied only in aqueous solutions.^{1,2} The origin of such sonochemistry is acoustic cavitation: the creation, growth, and implosive collapse of gas vacuoles in solution by the sound field. This collapse generates transient hot-spots with local temperatures and pressures of several thousand K and hundreds of atmospheres.³ Although the first observation of sonochemistry data back 50 years,¹ very few reports of the effects of ultrasound on nonaqueous liquids exist.⁴ A resurgence of interest in the chemical uses of ultrasound in homogeneous⁵⁻⁷ and heterogeneous⁸⁻¹⁰ systems may be noted. Much of this recent

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TABLE I: Products of *n*-Decane Sonolysis

product	rate, ^a nmol/min	product	rate, ^a nmol/min
H ₂	1610	1-C ₉ H ₁₀	135
CH ₄	350	C ₅ H ₁₂	21
C ₂ H ₂	260	1-C ₇ H ₁₂	68
C ₂ H ₄	345	C ₆ H ₁₄	28
C ₂ H ₆	46	1-C ₇ H ₁₄	44
C ₃ H ₄	22	C ₇ H ₁₆	16
C ₃ H ₆	297	1-C ₈ H ₁₆	42
C ₃ H ₈	32	C ₈ H ₁₈	9
1-C ₄ H ₈	188	1-C ₉ H ₁₈	21
C ₄ H ₁₀	47	C ₉ H ₂₀	3

^a Sonolysis completed under Ar at 25 °C in solution during irradiation. Rates are of total gas and liquid phase products: 20 mL gas volume, 10 mL liquid volume. All products detected are reported: gas and liquid detection limits are <3 and <1 nmol/min, respectively; error limits ±10%. Alkanes up to C₃₀H₆₂ would have been detected if present. Small amounts of CO₂ and CO are produced if O₂ is present.

work involves nonaqueous solvents, but no systematic study of the chemical effects of ultrasound on these has been made. We report here the first studies of the sonochemistry of and in alkane solvents. We find that alkanes do support acoustic cavitation and the associated sonochemistry, that this leads to carbon-carbon bond cleavage and radical rearrangements, and that the peak temperatures reached in such cavities are controlled by the vapor pressure of the solvent.

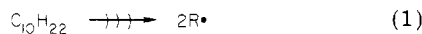
Experimental Section

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 total acoustic power ~100 W and acoustic intensities ~100 W/cm² at the horn's surface. Reactions were performed in a glass sonication cell under an Ar atmosphere, as described in detail elsewhere.^{5a,c}

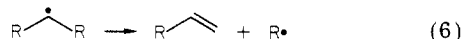
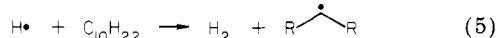
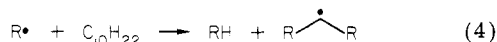
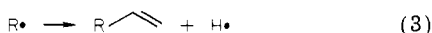
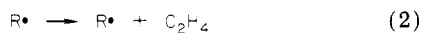
Product analyses were achieved by FT IR (Nicolet 7199 or MX-5), capillary (Varian 3700) and spherocarb packed-column (H.P. 5730A) vapor-phase chromatography, and UV-visible (Hitachi 100-80), as needed. Solvents were of highest available purity (spectrophotometric, gold label, 99%+) and used without further purification. Diphenylpicrylhydrazyl (DPPH) was multiply recrystallized, vacuum dried, and stored under Ar in the dark at -20 °C. Fe(CO)₅ (Alpha Ventron) was filtered or distilled imme-

Scheme I: Rice Radical Chain Mechanism^a

initiation:



propagation:



termination:



^a R• = terminal radical, R-CH₂-R = internal radical.

diately prior to use and protected from light.

Results and Discussion

The results of ultrasonic irradiation of decane are shown in Table I. This data represent the observed initial rates of formation. For less volatile products, rates are linear with time over 3000 min, but some diminution of observed rates for volatile products was noted due to small losses through the connected gas line. The principal products are H₂, CH₄, C₂H₂, and the smaller 1-alkenes. Very similar product distributions are observed for other *n*-alkanes. Useful comparisons may be drawn to other high-energy processes, including pyrolysis,^{11,12} vacuum UV photolysis,¹³ and radiolysis¹⁴ of alkanes. The products observed from the sonolysis of alkanes are consistent with the Rice radical chain mechanism demonstrated for alkane pyrolysis.¹¹ We postulate that the primary chemical step of the cavitation event is random C-C bond cleavage. The terminal radicals this produces can (1) eliminate ethylene yielding shorter chain primary radicals, (2) eliminate H• to yield 1-alkenes, or (3) abstract hydrogen from solvent to yield smaller alkanes and secondary radicals. The secondary radicals so generated undergo β-scission and produce 1-alkenes and primary radicals. This process is outlined in Scheme I.

In comparison to low-temperature pyrolysis¹¹ (~500 °C), sonolysis of alkanes generates very much larger relative yields of H₂, CH₄, and C₂H₂. These products are also produced by high-temperature (~1200 °C) shock tube pyrolysis,¹² which is consistent with the very high peak temperatures produced by acoustic cavitation. C₂H₂ is presumably produced (as in alkene pyrolysis^{11d}) from

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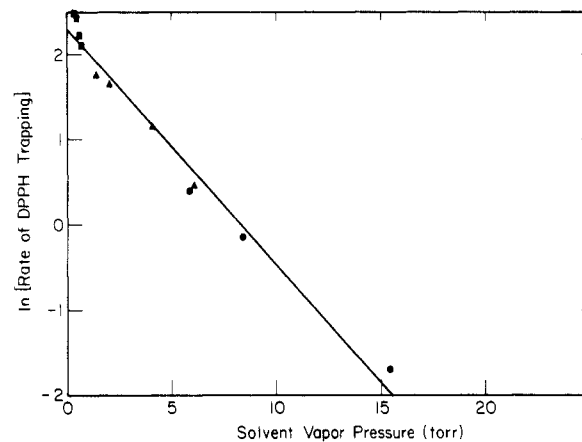


Figure 1. Rate of DPPH trapping vs. solvent system vapor pressure. In order of increasing vapor pressure: ■, decane, at 8, 11, 13, 15 °C; ▲, octane at -10, -5, 5, 11 °C; ●, heptane at -10, -5, 5 °C. Vapor pressures calculated from data in ref 19; rate in units of μM/min.

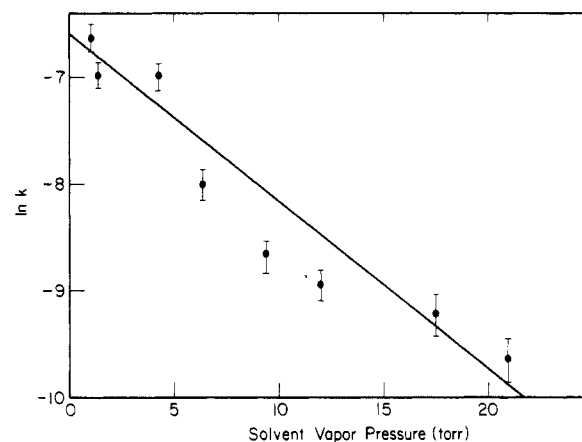


Figure 2. Rate of Fe(CO)₅ decomposition vs. solvent system vapor pressure at 25 °C. In order of increasing vapor pressure: decalin, decane, nonane, 0.22 mole fraction octane in nonane, 0.52 mole fraction octane in nonane, octane, 0.11 mole fraction heptane in octane, and 0.22 mole fraction heptane in octane. Vapor pressures calculated from data in ref 17, assuming ideal solution behavior. $d[\text{Fe}(\text{CO})_5]/dt = -k[\text{Fe}(\text{CO})_5]$, with k in units of s⁻¹; good first-order behavior was observed for 3.5 half-lives.

secondary reactions of C₂H₄ or C₃H₆. Addition of these to the sonication atmosphere did not significantly increase the yield of acetylene, however, due to the low local concentration such an ambient gas has in the cavitation event. Vacuum-UV photolysis of alkanes has been much less studied, but appears to involve principally unimolecular elimination of H₂. Since this would produce primarily internal olefins from *n*-alkanes, direct elimination of H₂ cannot be a significant pathway in alkane sonolysis. Radiolysis of alkanes (C_{*n*}H_{2*n*+2}) with ⁶⁰Co γ-rays or 4.5-MeV electrons yields¹⁴ principally H₂ and C_{*n*}H_{2*n*} alkenes, with smaller amounts of dimerized alkanes (C_{2*n*}H_{4*n*+2}) and shorter alkanes. This very different set of products derives primarily from unimolecular H₂ elimination,^{14b} although the involvement of radical and ionic species also contribute.

Two chemical dosimeters were examined in alkane solvent mixtures in order to gain further insight into the factors affecting acoustic cavitation: the bleaching of diphenylpicrylhydrazyl (DPPH) and the decomposition of Fe(CO)₅. DPPH is a well-studied stable free radical and has been extensively used as a radical trap¹⁵ even in so-

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nochemical reactions.^{5b,7c,16b} Confirming the radical chain mechanism for alkane sonolysis, DPPH completely inhibits the formation of the products reported in Table I. The sonochemical decomposition of $\text{Fe}(\text{CO})_5$ to $\text{Fe}_3(\text{CO})_{12}$ and Fe metal we have reported earlier.^{5a-c} For both of these dosimeters we observe good linear correlation between the log of the reaction rate and the vapor pressure of the solvent system as seen in Figures 1 and 2. This correlation can be predicted from simple hydrodynamic models of the cavitation process. Neppiras,^{3a} for example, derives the peak temperature generated during collapse of a gas filled cavity as

$$T_{\max} = \frac{T_0 P_a (\gamma - 1)}{Q} \quad (1)$$

where T_0 is the ambient temperature, P_a the acoustic pressure at initiation of collapse, γ the ratio of specific heats, and Q the gas pressure in bubble at initiation of collapse. In the case of vapor-filled cavities, we may take $Q = P_v$, the vapor pressure of the solvent.¹⁶ If we assume that the sonochemical reactions follow Arrhenius behavior ($k = A e^{-E_a/RT_{\max}}$), then

$$\ln k = \ln A - \frac{E_a}{RT_0 P_a (\gamma - 1)} P_v \quad (2)$$

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 cavitation collapse. Figures 1 and 2 do demonstrate, however, a reasonable

correlation of $\ln k$ with P_v for very different sonochemical reactions.

Alternatively, Sehgal et al.^{7c} have shown that the total free energy of cavity formation ($\Delta \tilde{A}$) is related to the vapor pressure (P_v) and the ambient pressure (P_0) as

$$\Delta \tilde{A} = RT \ln (P_v/P_0) \quad (3)$$

If one assumes that the free energy *release* during cavitation collapse is related to the free energy of cavity *formation*, then a correlation between $\ln k$ and $\Delta \tilde{A}$ should be found. Qualitatively we find this to be the case only over a limited range in P_v .^{5f}

Conclusion

Thus we have demonstrated a facile means to control the conditions generated during acoustic cavitation: solvent vapor pressure. As one diminishes the solvent volatility, the intensity of cavitation collapse, the maximum temperature reached, and the rate of reaction all increases. The sonochemical reactions examined here, then, have the curious property of *decreasing* rates with increasing ambient temperature, due to the increased solvent vapor pressure. As we have noted elsewhere,^{5a} the solvent control exerted on sonochemical pathways can be extreme: the change in vapor pressure from decane to heptane can change relative product yields by a hundredfold for reaction pathways which differ significantly in their activation energies.

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Registry No. *n*-Decane, 124-18-5.

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