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SONOCHEMISTRY OF ACETONE AND ACETONITRILE IN AQUEOUS SOLUTIONS. A SPIN TRAPPING STUDY

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The 50 kHz sonolysis of argon-saturated water-acetone and water-acetonitrile mixtures was studied by EPR and spin trapping with 3,5-dibromo-4-nitrosobenzenesulfonate over a wide range of solvent composition. For both systems a single maximum was observed for the spin adduct yield of methyl radicals and of the radicals formed by H-abstraction from acetone and acetonitrile. These results combined with previous studies of water-methanol and water-ethanol mixtures indicate that the greater the vapor pressure of the volatile organic component, the lower the concentration of organic solute at which the maximum radical yield occurs. Methyl radicals from acetone are formed by C−C bond scission in the collapsing argon bubbles. For acetonitrile, C−H bond scission at high temperature is followed by H-addition to the triple bond and the decomposition of this intermediate radical to form methyl radicals. Since Anbar has shown (Science 161, 1343, 1961) that sonoluminescence and acoustic cavitation occur during the impact of liquid water on water with linear velocities similar to those of collapsing ocean waves, the sonochemistry of nitriles is of interest to chemical evolution studies.

KEY WORDS: Sonochemistry, spin trapping, electron spin resonance, acoustic cavitation, acetone, acetonitrile.

INTRODUCTION

Acoustic cavitation involves the formation, growth and implosive collapse of gas bubbles in liquids.[1,2] The very high temperatures (5000 K) and pressures in local hot spots[3,4] with lifetimes of a few microseconds lead to the thermal dissociation of water vapor into H atoms and OH radicals[5,6] and to pyrolysis products from volatile organic solutes. The H atoms and OH radicals which escape into the bulk of the solution at ambient temperature react with solutes to yield products identical to those observed in the radiation chemistry of dilute aqueous solutions of organic solutes.[7]

Sonochemistry is a probable pathway for the formation of complex organic compounds in the primordial methane-saturated ammoniated ocean.[8] The linear velocity of water in collapsing ocean waves has been estimated to be about 5 m sec^{-1} and above. This is the range of velocities for which Anbar has shown by water-on-

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water impact that sonoluminescence and the associated sonochemistry will occur.[9] Previous studies have shown that the action of ionizing radiation on aqueous oxygen-free solutions of propionitrile leads to the formation of a mixture of compounds of interest to chemical evolution studies, including compounds which on hydrolysis lead to 11 protein and non-protein amino acids.[10] The sonolysis of aqueous nitriles is therefore of interest for studies related to chemical evolution.[10,11] The sonochemistry of water-acetonitrile and water-acetone mixtures is also relevant because of the increasing use of ultrasound in synthetic organic chemistry.[12]

In the present work, the sonochemistry of aqueous solutions of acetone and acetonitrile were investigated over a wide range of solute concentrations by EPR and spin trapping methods.[13] We have found previously that 3,5-dibromo-4-nitrosobenzenesulfonate is a particularly suitable spin trap for aqueous sonolysis studies.[14] The sulfonate group anchors the spin trap in the aqueous phase and several carbon-centered radical adducts show sufficiently detailed spectra to allow the identification of the trapped radical.

The results of the present work combined with previous studies[15,16] indicate that the greater the vapor pressure of the volatile organic solute, the lower the concentration at which the maximum radical yield is observed.

MATERIALS AND METHODS

Chemicals

The spin trap 3,5-dibromo-4-nitrosobenezenesulfonate, sodium salt (DBNBS) was purchased from Sigma Chemical Co., and the corresponding 2,6-deuterated analogue was obtained from Dr. R.M. Chedekel (Melanin Laboratories, The Johns Hopkins Laboratories, Baltimore, Maryland). Reagent grade acetone, acetonitrile and CD_3CN were obtained from Aldrich Company. H_2O_2 (30%) was obtained from Fischer Scientific Company. MilliQ reagent water was used for all of the experiments.

Sonolysis Experiments

A sample solution (3 ml) containing DBNBS as the spin trap was placed into a specially designed Pyrex tube fixed in the center of the sonication bath by means of a plastic template (Bransonic 1200), frequency approximately 50 kHz. The level of the liquid inside the tube was the same as that of the water in the sonication bath (temperature 25°C). The sample solution was bubbled with argon (flow rate, 100 ml/min.) through a fine syringe needle attached to a teflon tube immersed in the liquid. The argon was pre-equilibrated with 200 ml of a solution of the same composition in a bubbling tower to avoid depletion of the volatile component during sonolysis. The usual sonication time was 10 minutes.

Photolysis Experiments

H_2O_2 (30%) at a concentration of 50 μL/mL was added to the sample solutions containing the spin trap prior to photolysis. The photolysis experiments were carried out at room temperature using a Schoeffel 1000 W Xe lamp coupled to a Schoeffel grating monochromator. The spin adducts were generated by UV irradiation

at 275 ± 10 nm of the argon-saturated solutions in an EPR quartz flat cell (60 × 10 × 0.25 mm) placed directly in the EPR cavity. The illumination time was usually between 1 and 2 min.

EPR Measurements

The EPR spectra were recorded on a Varian E-9 X-band spectrometer operating at 100 kHz modulation frequency and 9.5 GHz microwave frequency. The microwave power was kept at 20 mW. Immediately after sonolysis, the sample was transferred into a quartz flat cell for EPR measurement. The EPR spectra were recorded about 1 min after sonolysis, and repeatedly scanned to estimate decay rates of the spin adducts. To estimate relative radical yields, the observed EPR signal heights of different spin adducts were corrrected for peak-to-peak widths and for the statistically weighted number of lines in each spectrum.

RESULTS

Sonolysis of argon-saturated CH_3COCH_3-H_2O (20:80, v/v) in the presence of DBNBS (8.2 mM) produced three spin adducts of DBNBS due to $\dot{C}H_3$, CH_3-$CO\dot{C}H_2$ and most likely an unidentified $\rangle\dot{C}H$ radical (Figure 1). The DBNBS-CH_3 spectrum consists of six groups of lines. This spectrum is due to a primary nitrogen triplet (a_N = 1.45 mT). Each line of this triplet is further split into a 1:3:3:1 quartet by three equivalent protons (a_{3H} = 1.33 mT). An additional splitting of 0.075 mT due to two equivalent meta hydrogens of the spin trap is also observed. This spin adduct has been observed previously in different solvents.[15,16]

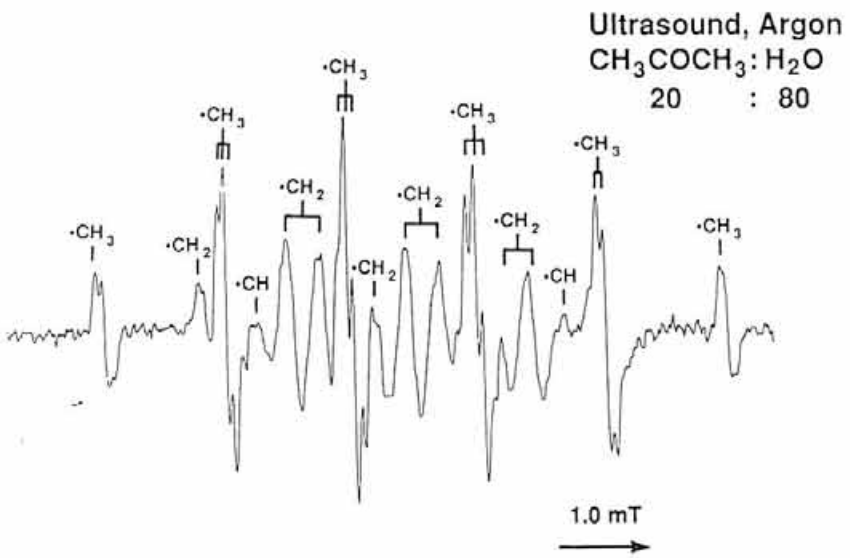

FIGURE 1 EPR spectrum of spin-trapped radicals immediately after sonolyis of an argon-saturated acetone-water mixture (20:80, v/v) in the presence of 8.2 mM DBNBS.

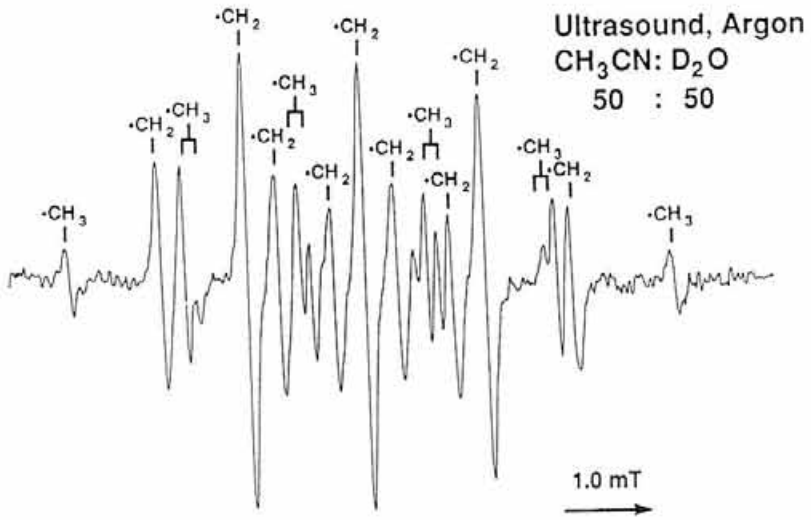

FIGURE 2 EPR spectrum of spin-trapped radicals immediately after sonolysis of an argon-saturated acetonitrile-D_2O (50:50, v/v) in the presence of 9.3 mN DBNBS.

The DBNBS-CH_2COCH_3 adduct was also present (lines labeled CH_2 in Figure 1) and could be identified by comparison with the EPR spectrum obtained immediately after γ radiolysis of an N_2O-saturated solution of 50 mM acetone (not shown). This spectrum is due to a nitrogen triplet ($a_N = 1.35$ mT) further split into a 1:2:1 doublet due to two equivalent hydrogens ($a_H = 0.95$ mT).

Sonolysis of argon-saturated CH_3CN-D_2O (50:50 v/v) produced two spin adducts of DBNBS due to $\dot{C}H_3$ and $\dot{C}H_2CN$ (Figure 2). The DBNBS-CH_2CN spectrum (lines labeled CH_2 in Figure 2) was identified by comparison with the EPR spectrum obtained by the 275 nm photolysis of CH_3CN (20:80, v/v) containing 160 mM hydrogen peroxide solution and DBNBS-d_2 (Figure 3a). This spectrum is due to a primary nitrogen triplet ($a_N = 1.33$ mT) further split into a 1:2:1 triplet ($a_H = 0.98$ mT).

This assignment was confirmed by photolysis of CD_3CN-D_2O (20:80, v/v) in the presence of DBNBS-d_2 and 160 mM D_2O_2. The spectrum of the DBNBS-d_2-CD_2CN spin adduct generated in this experiment is shown in Figure 3b. A nitrogen triplet ($a_N = 1.33$ mT) is further split into a quintet of lines in the intensity ratio of 1:2:3:2:1 due to two equivalent deuterium nuclei (I = 1) with $a_D = 0.15$ mT. This is in agreement with the ratio of the gyromagnetic ratios of hydrogen and deuterium nuclei of 6.51.

The effect of acetone and acetonitrile concentrations on the radical yields is shown in Figures 4 and 5. Radical yields increase with increasing acetone and acetonitrile concentration, reach a single maximum and then decrease. A similar dependence of radical yield on methanol concentration was observed previously.[15] However, for ethanol two maxima were observed, the first at ~2 M and the second at ~10 M ethanol. The initial maximum for the $\dot{C}H_3$ and $\dot{C}H_2CH_2OH$ adducts can be attributed to changes of spin trapping efficiency at different solvent compositions.[16] The second maximum is due to acoustic cavitation.

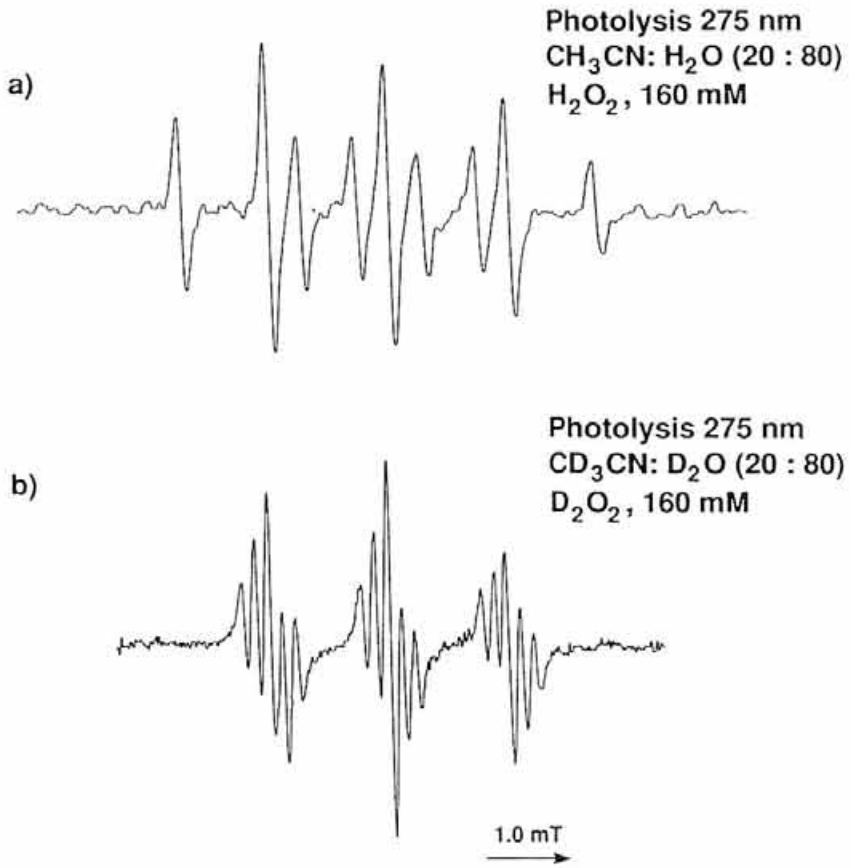

FIGURE 3 EPR spectra of spin-trapped radicals after photolysis at 275 nm of an acetonitrile-water mixture (20:80, v/v) in the presence of 10 mM DBNBS-d_2. (a) CH_3CN-H_2O, 1.6 mM H_2O_2, (b) CD_3CN-D_2O, 1.6 mM D_2O_2.

DISCUSSION

In the sonochemistry of aqueous solutions of volatile solutes, reactions occur in three different regions.[17,18] During the implosive collapse of cavitation bubbles, the very high temperatures (of the order of 5000 K) and pressures (several hundred atmospheres) result in typical gas phase pyrolysis reactions.[17,18] In this region thermal dissociation of water leads to the formation of hydrogen atoms and hydroxyl radicals.[5,6]

The second region is the interfacial region between the collapsing gas bubbles and the bulk solvent, where temperatures are lower than in the interior of the gas bubbles, radical concentrations are relatively high, and solutes with high hydrophobicity tend to accumulate preferentially.[19,7]

The third region is the bulk of the solution at ambient temperature. The radicals which were produced in the interior of the gas bubbles and did not recombine or were

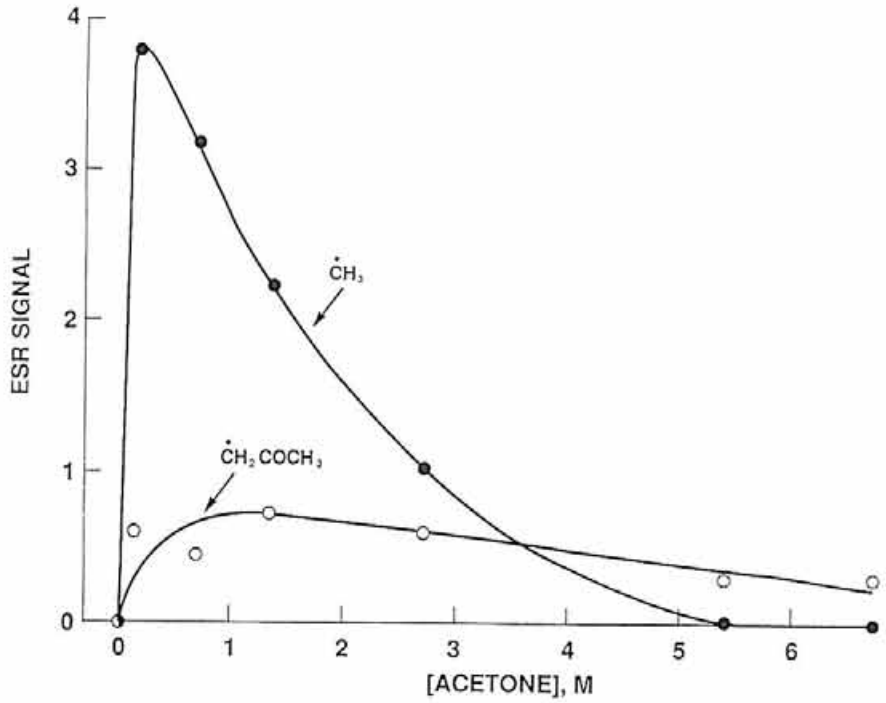

FIGURE 4 Effect of acetone concentration on the EPR signal intensity (arbitrary units) of DBNBS-CH_3 adduct (•) and DBNBS-CH_2COCH_3 adduct (○) obtained by sonolysis (10 min) of argon-saturated CH_3COCH_3-H_2O mixtures in the presence of DBNBS (8.2 mM).

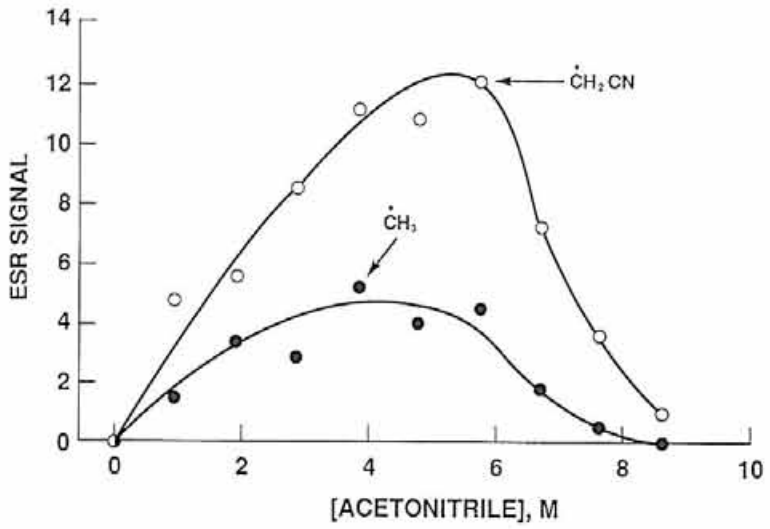

FIGURE 5 Effect of acetonitrile concentration on the EPR signal intensity (arbitrary units) of DBNBS-CH_3 adduct (•) and DBNBS-CH_2CN (○) obtained by sonolysis (10 min) of argon-saturated CH_3CN-D_2O mixtures in the presence of DBNBS (9.3 mM).

SCHEME I
Sonolysis of CH_3COCH in H_2O

A. Reactions of H and OH similar to those observed in aqueous radiation chemistry

$$H_2O \xrightarrow{)))} H + OH \quad (1)$$
$$OH + CH_3COCH_3 \longrightarrow H_2O + CH_3C\dot{O}CH_2 \quad (2)$$
$$OH + CH_3COCH_3 \longrightarrow (CH_3)_2C(OH)\dot{C}H_2 \quad (3)$$
$$H + CH_3COCH_3 \longrightarrow H_2 + CH_3C\dot{O}CH_2 \quad (4)$$
$$H + CH_3COCH_3 \longrightarrow (CH_3)_2\dot{C}(OH) \quad (5)$$

B. Pyrolysis of Acetone

$$CH_3COCH_3 \longrightarrow 2\dot{C}H_3 + CO \quad (6)$$
$$\dot{C}H_3 + CH_3COCH_3 \longrightarrow CH_4 + \dot{C}H_2COCH_3 \quad (7)$$
$$CH_3C\dot{O}CH_2 \longrightarrow \dot{C}H_3 + CH_2 = C = O \quad (8)$$
$$CH_3C\dot{O}CH_2 + \dot{C}H_3 \longrightarrow CH_3COCH_2CH_3 \quad (9)$$
$$CH_3COCH_2CH_3 + \dot{C}H_3 \longrightarrow CH_4 + CH_3C\dot{O}CHCH_3 \quad (10)$$
$$CH_3CO\dot{C}HCH_3 \longrightarrow \dot{C}H_3 + CH_3 - CH = C = O \quad (11)$$

not scavenged in the interfacial region and have escaped into the bulk of the liquid react with solutes with kinetics similar to those observed in dilute aqueous radiation chemistry and yield the same products.[20,7]

Hence, an insight into the sonochemistry of aqueous solutions of volatile organic solutes can be attained by considering, first, pyrolysis studies of the organic solute in the vapor phase which are analogous to the pyrolysis reactions in the collapsing gas bubbles. Second, from the known aqueous radiation chemistry of dilute solutions of the organic solute, we can predict the sonochemical reactions of the H atoms and OH radicals which escape into the bulk of the solution and react with the solute at ambient temperature and pressure.

The aqueous radiation chemistry of acetone[21] and the pyrolysis of acetone vapor[22] have been studied previously and the relevant reactions are summarized in Scheme I.

At room temperature, H atoms and OH radicals react with acetone to form $CH_3C\dot{O}CH_2$ radicals (reactions 2 and 14). However, methyl radicals are formed only by pyrolytic scission of the carbon-carbon bond (reaction 6), with possible contributions from the radical decomposition reactions 8 and 11. The spin adduct of the $\rangle\dot{C}H$ radical observed in sonolysis and labeled CH in Figure 1 could possibly be explained by reaction 10.

For acetonitrile, the aqueous radiation chemistry was investigated by Draganić *et al.*,[23] and pyrolysis at high temperatures below reflected shocks was studied by Lifshitz *et al.*[24] and are summarized in Scheme II.

In the sonolysis of aqueous CH_3CN solutions, methyl radicals are formed as a result of H atom addition to the triple bond and the C-C bond scission of the resulting radical (reaction 12). $\dot{C}H_2CN$ radicals have been shown to be formed in the initiation step of the pyrolysis reaction in the 1350–1950 K range (reaction 17) or by abstraction reactions 13 and 16.

Several factors influence the extent of acoustic cavitation and hence the sonochemical radical yields.[1] In the bulk solution, cavitation activity is decreased by high viscosity, low surface tension, high vapor pressure and low sound speed. In the gas phase, sonolytic yields are decreased when the gas mixture in the collapsing cavitation bubble has a low value of γ (Cp/Cv) and high termal conductivity since bubble collapse is not completely adiabatic.[1,25] Since $\gamma = 1.67$ for argon and 1.20

SCHEME II
Sonolysis of $CH_3 - C{\equiv}N$ in H_2O

A. Reactions of H and OH similar to those observed in aqueous radiation chemistry

$$H_2O \xrightarrow{))\!)} H + OH \quad (1)$$

$$H + CH_3 - C{\equiv}N \longrightarrow [CH_3 - \dot{C}H - C{\equiv}N \text{ or } CH_3 - \dot{C} = NH] \quad (12)$$

$$\downarrow$$

$$\dot{C}H_3 + HC{\equiv}N$$

$$H + CH_3 - C{\equiv}N \longrightarrow H_2 + \dot{C}H_2 - C{\equiv}N \quad (13)$$

$$\dot{C}H_3 + CH_3 - C{\equiv}N \longrightarrow CH_4 + \dot{C}H_2 - C{\equiv}N \quad (14)$$

$$OH + CH_3 - C{\equiv}N \longrightarrow [CH_3 - C(\dot{O}H) = N \text{ or } CH_3 - \dot{C} = NOH] \quad (15)$$

$$OH + CH_3 - C{\equiv}N \longrightarrow H_2O + \dot{C}H_2 - C{\equiv}N \quad (16)$$

B. Pyrolysis at high temperature behind reflected shocks.

$$CH_3 - C{\equiv}N \longrightarrow \dot{C}H_2 - C{\equiv}N + H \quad (17)$$

for polyatomic molecules, the effective γ for the gas phase of the cavitation bubbles depends on the composition of the gas phase and hence on the mole fraction of the volatile solute and its vapor pressure. The significance of the value of γ of an ideal gas on the final collapse temperature after adiabatic compression is shown by the following calculation[4]. For a gas initially at 298 K and for compression ratios (initial volume of gas bubble/final volume) of 2, 4, and 10, respectively, the final temperatures for argon ($\gamma = 1.67$) are 945 K, 3007 K and 13,892 K, respectively. However, for a polyatomic gas ($\gamma = 1.20$), the corresponding temperatures are 682 K, 1568 K, and 4707 K.

In general, the plots of sonolysis product yield against solute concentration exhibit a single maximum. The initial increase is due to the increasing fraction of volatile reactant in the collapsing argon bubbles, while the subsequent decrease results mostly from the lower ratio of specific heats of the argon bubble, as the monoatomic gas ($\gamma = 1.67$) is mixed with increasing amounts of the polyatomic solute. Combining the current results with previous studies of methanol[15] and ethanol,[16] it is found that the greater the vapor pressure of the organic solute, the lower the concentration of organic solute in water at which the maximum of the methyl radical yields occurs (Table 1). Thus, for acetone with a vapor pressure of 210 mm at 25°C, the maximum $\dot{C}H_3$ yield occurs at $\leqslant$0.1 M, while for ethanol with a vapor pressure of 57 mm, the maximum is found for 10 M solutions.

These results are consistent with the work of Suslick *et al*,[26] who found that the rates of bleaching of the radical trap diphenylpicrylhydrazyl and the rates of decomposition of $Fe(CO)_5$ in many organic liquids is primarily dependent on solvent

TABLE I

	Vapor pressure at 25°C (mmHg)	Conc.(M) in H_2O at maximum sonolysis yield of $\cdot CH_3$
CH_3COCH_3	210	$\leqslant$0.1
CH_3OH	120	4
CH_3CN	90	4
CH_3CH_2OH	59	10

vapor pressure. With increasing vapor pressure, the intensity of cavitational collapse, the maximum temperature reached and the rates of reaction all decrease. A good correlation was found between log (sonochemical reaction rate) and the solvent vapor pressure.[26]

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