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Sonolysis Studies of Alcohols in Aqueous Solutions by Gaseous Products Analysis

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Synopsis. Sonolysis studies of alcohol–water mixtures were carried out for CH_3OH, C_2H_5OH, n-C_3H_7OH, and i-C_3H_7OH by analyzing the gaseous products of CH_4, C_2H_6, C_2H_4, C_2H_2, and C_3H_6. By comparing the product distributions which depended on the four alcohol–water mixtures it was found that alcohols decay in a similar manner as in the pyrolysis of alcohols at high temperatures and that sonolysis progresses through radical reactions.

Reactions in ultrasound-irradiated aqueous solutions have been observed in many reaction systems.[1] Recently, the sonolysis of a CH_3OH–water system was investigated by two groups.[2,3] Methyl radicals and CH_2OH radicals were observed to appear in the sonolysis by an ESR spin trapping method.[2] The product distribution in the sonolysis[3] was found to be quite similar to that in the combustion of CH_3OH in the gas-phase at high temperatures.[4] Based on these results, a reaction sequence is featured in which CH_3OH decays first by breaking the C–O bond, and then decays through radical reactions.

An ultrasound-initiated reaction in an aqueous solution is considered to occur due to the generation of hot-spots of several thousand K.[1,5] The mechanism of hot-spots generation could be explained as follows. Ultrasound produces cavitation gas bubbles due to its sound-wave-action in the solution. The collapse of bubbles adiabatically compresses the vapor in the bubbles, thus heating it.

We paid attention to the sonolysis of other C_2 and C_3 alcohols, and compared them with that of CH_3OH. They are expected to decay not only by breaking the C–O bond, like CH_3OH, but also by breaking other C–C bonds. Since there may arise various radicals having different reactivities, the product distribution, if observed, may show a distinctive dependence on the alcohols used. We tried to explain the distribution based on the reactivities of molecules and radicals at high temperatures.[6,7]

Experimental

The experimental system of sonolysis comprises a sample cell, a gas-circulating system, and a gas-chromatograph. A schematic diagram of this system is shown in Fig. 1.

The cell used was a gas-absorbing bottle (Kinoshita, KR-G-250, inner volume: 250 ml). The input and output glass-tubes of the bottle were improved so as to be connectable to a gas-circulating system with a vacuum-tight connector (Cajon, Ultra-Torr Fittings). Gas circulation was achieved with a tubing pump system (Masterflex, PA-31). The gas-circullating system had a gas-sampling port of septum for carrying out gas-chromatographic analyses. The system was also connected to an Ar gas cylinder; degassing and bubbling of the solution were carried out with Ar for 15 min before sonication. During the degassing and bubbling, the gas-sampling port was opened and residual gas was purged out. The cell was placed in the center of the sonication bath (Bransonic 3200; frequency 50 kHz; output power 120 W) and a few mm above the bottom of the bath. After a sonication time of 20 min, the sampled gas (100 µl) was analyzed using a gas-chromatograph (Hitachi, 263-50) combined with a chromato-integrator (Hitachi, D-2500). The running conditions of the chromatograph were: Column; Unipak-S, detector; FID, carrier gas (He) flow rate; 40 ml min^{-1}, temperatures of injection port and detector; 110 °C, and oven temperature; 60 °C.

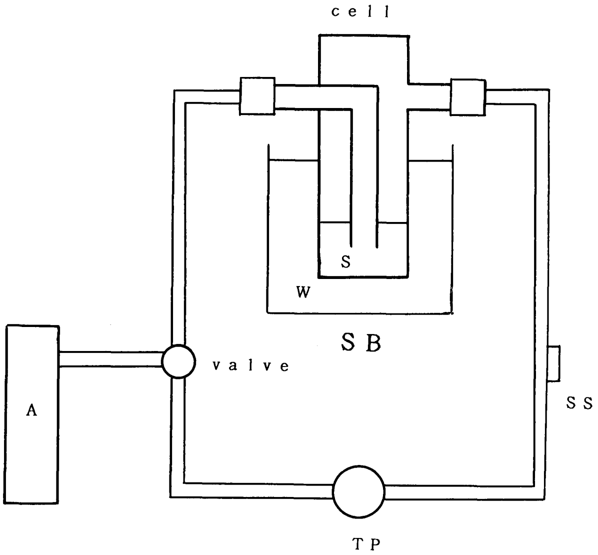

Fig. 1. Schematic diagram of the apparatus. SB: Sonication bath, TP: Tubing pump, SS: Septum for sampling, S: Alcohol-water solution, W: Water, A: Ar-gas container.

Alcohol solutions (100 ml) were prepared by diluting with distilled water. The alcohols used were CH_3OH (99.6% pure, Wako), C_2H_5OH (99.5% pure, Wako), n-C_3H_7OH (99.5% pure, Kantou Kagaku) and i-C_3H_7OH (99.5% pure, Kantou Kagaku). The Ar used was 99.999% pure (Nippon Sanso). The alcohols and Ar were used without further purification.

Results and Discussion

The reaction conditions of the vapor in the cavitation bubbles formed by ultrasound change their dependence on such physical parameters as the heat capacity, heat conductivity and viscosity of the solutions and the gases used. In the present experiment, the reaction conditions were different in the four alcohol–water mixtures. Although many ambiguities are present in the reaction conditions for sonication, reproduction of the measured species concentrations was found to be very good in the present experimental system.

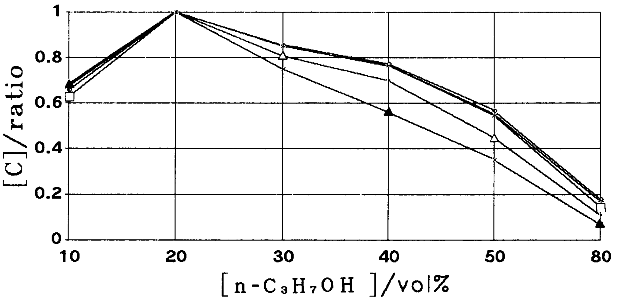

Fig. 2. Relative yields vs. composition of n-C_3H_7OH in water solution (vol%). The concentration of products at 20 vol% solution of n-C_3H_7OH were taken to be 1. Symbols used are: Square=C_2H_6, Triangle=C_3H_6, Filled triangle=C_2H_2. CH_4 and C_2H_4 are almost on the same line.

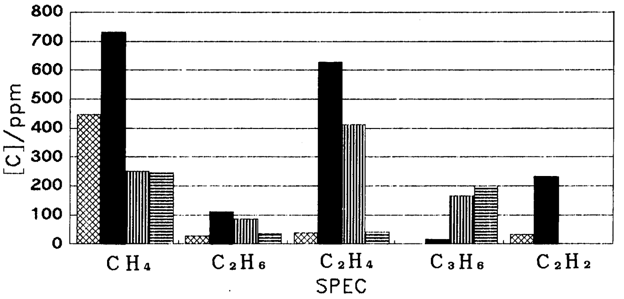

Fig. 3. Product distribution in sonolysis of 20 vol% solution of alcohols. Each group of species has four bars which show the concentrations produced in the four alcohol–water mixtures. The alcohols are, from left to right of the four bars, CH_3OH, C_2H_5OH, n-C_3H_7OH, i-C_3H_7OH, respectively. Each bar is an average of measurement of three times. [C_3H_6] in the CH_3OH mixture and [C_2H_2] in the n-C_3H_7OH and i-C_3H_7OH mixtures are small and are not shown in the figure.

We first studied the dependence of the alcohol concentration on the product distribution for the four different kind of alcohols. As shown in Fig. 2 for the n-C_3H_7OH case, the product distribution seems to change similarly, and its maximum appears at low alcohol concentrations, rather than at high ones. Similar relations were also obtained for the other three alcohols, and the existence of maximum points was confirmed. Such a composition dependence in the sonolysis of alcohols is in accordance with that reported for CH_3OH–water mixtures.[2,3]

Since the alcohol vapor concentration in bubbles is expected to increase with an increase in that of the solution, the yield of hydrocarbons increases first, accordingly. The amount of product depends on that of reactant as well as on the reaction temperature. Therefore, a decrease in the products at higher alcohol concentrations must be due to a decrease in the temperature. Studies by Neppiras[8] and Flynn[9] showed that the attainable maximum temperature (T_m) of the vapor in bubble cavitation is given by $T_m \simeq T_0 P_a(\gamma - 1)/P_v$, where T_0 is the ambient temperature (293±5 K), P_a the acoustic pressure at the initiation of collapse, γ the specific heat ratio of vapor, and P_v the vapor pressure of the solution. P_a can be assumed to be constant in the present case, since it mainly depends on the experimental setup of sonolysis. The composition-dependent variables are the γ of the vapor and the P_v of the solution. The γ value decreases with an increase in the heat capacity (C_p). The C_p (J mol^{-1} K^{-1}) values of water and alcohols at 300 K are 33.5 (H_2O), 43.9 (CH_3OH), 65.7 (C_2H_5OH), 87.8 (n-C_3H_7OH), and 89.9 (i-C_3H_7OH).[10] Since the C_p values of alcohols are larger than that of water, the γ of the vapor decreases with an increase in the alcohol concentration of vapor. The vapor pressures (mmHg, 1 mmHg=133.322 Pa) at 300 K are 24 (H_2O), 126 (CH_3OH), 59 (C_2H_5OH), 20 (n-C_3H_7OH), and 43 (i-C_3H_7OH).[11] Except for the P_v of n-C_3H_7OH, the P_v values of alcohols are larger than that of water, and the P_v values of the solutions become large at high alcohol concentrations. The decrease of γ and the increase of P_v play roles to decrease T_m, and the yields of products consequently decrease. Accordingly, the variations of the alcohol concentration as a reactant and the T_m value give a maximum in the products vs. alcohol concentration curves in Fig. 2.

Figure 3 shows the product distribution observed in the four alcohol–water systems. The selected concentration of alcohols was 20 vol% so as to gain maximum of products. By accepting the reaction mechanism proposed for the sonolysis of CH_3OH–water mixture,[2,3] the alcohols can be considered to decay as follows. The following mechanism is based on a study of CH_3OH pyrolysis above 1000 K:[4]

$$\mathrm{ROH} \longrightarrow \mathrm{R} + \mathrm{OH}, \tag{1}$$

$$\mathrm{C_2H_5OH} \longrightarrow \mathrm{CH_3} + \mathrm{CH_2OH}, \tag{2}$$

$$\mathrm{C_3H_7OH} \longrightarrow \mathrm{CH_3} + \mathrm{C_2H_4OH}, \tag{3}$$

and

$$\mathrm{C_3H_7OH} \longrightarrow \mathrm{C_2H_5} + \mathrm{CH_2OH}. \tag{4}$$

Hence, R is the alkyl radical and C_3H_7OH exhibits two isomers. The produced alkyl radicals react with alcohols and yield alkanes as follows:

$$\mathrm{CH_3} + \mathrm{ROH} \longrightarrow \mathrm{CH_4} + \mathrm{R'OH} \tag{5}$$

and

$$\mathrm{C_2H_5} + \mathrm{ROH} \longrightarrow \mathrm{C_2H_6} + \mathrm{R'OH}, \tag{6}$$

where R′ indicates biradicals. The above mechanism explains why CH_4 as well as C_2H_6 increase with an increase in the alkyl radicals produced.

We next paid attention to the yield of CH_4 produced in the four alcohol-water mixtures. Figure 3 shows that the order of the yield was $C_2H_5OH > CH_3OH > i$-$C_3H_7OH \simeq n$-C_3H_7OH. The inequality $C_2H_5OH > CH_3OH$ arises from the fact that the bond dissociation energy of C–C (356 kJ mol^{-1}) is smaller than that of C–O (377 kJ mol^{-1})[12] and that the C–C bond breaks more easily than does the C–O bond. Although methyl radicals are expected to be easily produced in i-C_3H_7OH and n-C_3H_7OH mixtures (based on the same point of view), the [CH_4] produced in these two mixtures was not so large as those in the other two mixtures of CH_3OH and C_2H_5OH. This result does not originate from the difference of the bond dissociation energy between C–C and C–O, nor from the difference of the γ values between the alcohol–water mixtures. The γ values of the four alcohol–water mixtures are similar. Since the physical parameters (viscosity, surface tension, and heat conductivity) of the four alcohols are not very different each other,[11] we must find some other reasons undiscovered heretofore.

Except for the methyl radicals, alkyl radicals further decompose by themselves as follows:

$$C_2H_5 \longrightarrow H + C_2H_4, \tag{7}$$

$$C_3H_7 \longrightarrow CH_3 + C_2H_4, \tag{8}$$

and

$$C_3H_7 \longrightarrow H + C_3H_6. \tag{9}$$

The methyl radicals produced by Reaction (8) play roles in Reaction (5) to produce CH_4. As was discussed first, the temperature gained by sonication changes in dependence on the composition of the alcohol–water mixtures as well as kinds of alcohols examined. Thus, the difference in the productivity of a species depending on that of the bond dissociation energy is very distinctive in the same alcohol–water mixtures. In the C_2H_5OH case, methyl radicals are expected to be produced more than are ethyl radicals; thus, through Reactions (5) and (7), CH_4 and C_2H_4 could be produced. If $[CH_3] \simeq [C_2H_5]$, the production ratio of $[CH_4]/[C_2H_4]$ by Reactions (5) and (7) is given by $k_5[C_2H_5OH]/k_7$, where k_7 is a high-pressure-limit rate constant, since sonolysis could occur at very high pressures, e.g., 500 atm.[5] Referring to the reported values,[13,14] $k_5 = 2\times10^{10}$ cm^3 mol^{-1} s^{-1} and $k_7 = 3\times10^7$ s^{-1} were evaluated at 1500 K. Equal values for $k_5[C_2H_5OH]$ and k_7 could be given at $[C_2H_5OH] = 1.5\times10^{-3}$ mol cm^{-3} = 0.2 atm by assuming the ideal-gas law. This condition could be easily attained since sonolysis may occur at very high pressures.[5] Thus, $k_5[C_2H_5OH]$ is much larger than k_7 and $[CH_4] > [C_2H_4]$ could be established. A difference in the reactivities can also be seen in the similar alcohols used. Since the T_m values in the two C_3H_7OH–water mixtures are expected to be similar, the differences in the productivities of C_2H_4 and C_3H_6 between the two C_3H_7OH–water mixtures could be explained based on the β-bond breaking rule for the two propyl radicals produced by Reaction (1) as follows. Propyl radicals yield methyl radicals and C_2H_4 by Reaction (8), whereas, isopropyl radicals yield hydrogen atoms and C_3H_6 by Reaction (9).[6,7]

In conclusion, the product distribution of small hydrocarbons given by the sonication of alcohol–water mixtures could be explained based on knowledge concerning the gas-phase pyrolysis of alcohols. In order to obtain greater insight into sonication, the reactions between alcohols and H-atoms or OH-radicals, given by the decompositions of alcohols and of H_2O, must be investigated; further, species having oxygen atoms must be observed.

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