Isotopic Exchange in the Sonolysis of Aqueous Solutions Containing D₂ and CH₄

Edwin J. Hart, Ch.-Herbert Fischer, and Arnim Henglein*

Hahn-Meitner-Institut Berlin, Bereich Strahlenchemie, 1000 Berlin 39, Federal Republic of Germany (Received: March 6, 1987)

Water was insonated under an argon atmosphere which contained various amounts of a D2-CH4 (2:1 vol %) mixture. Maximum yield for the formation of CH₃D, CH₂D₂, CHD₃, and CD₄ was observed at 40 vol % argon. Ethane, ethylene, acetylene, and many higher hydrocarbons were also produced with about one third of the deuteriated methane yield. In addition, some H/D exchange took place between D₂ and H₂O, and H₂ was formed from water. Carbon monoxide and carbon were produced, too. A mechanism involving free radicals and atoms is discussed to explain these observations.

Introduction

During the past few years interest in the sonolysis of aqueous solutions has been focussed on gas reactions that occur in cavitation bubbles. The reactions studied include the decomposition of methane,¹ carbon dioxide,¹ nitrous oxide,^{1,2} and ozone,³ as well as isotopic exchange in the systems $D_2-H_2O_1^4$ HD- $H_2O_1^5$ ^{18,18} $O_2-H_2^{16}O_1^6$ and ^{14,14} $N_2^{-15,15}N_2^7$ in $H_2O_2^{-16}$. For example, methane in argon bubbles is rapidly converted into hydrocarbons of longer chain lengths and hydrogen.¹ It is now found that isotopic exchange in the CH₄ molecule also occurs to an appreciable extent in D_2 -CH₄ mixtures in addition to the decomposition of methane.

As in the previous work the reacting gas mixture of deuterium and methane was diluted by various amounts of argon and the yield of the products determined after the insonation of water under this D₂-CH₄-Ar atmosphere. Some experiments were also carried out on the sonolysis of deuteriated methane, CD4, in argon bubbles. The reactions are initiated by the high temperatures which exist for a very short time during the adiabatic compression phase and collapse of the gas bubbles.8

Experimental Section

The ultrasound was generated by a quartz oscillator of 300 kHz and the intensity was about 2 W/cm². The irradiation vessel was described previously as well as the gas analysis by Van Slyke techniques and mass spectrometry.⁴ In the present case, a 60-cm³ irradiation cell with 37.5 mL of water was irradiated. After irradiation, about 15 cm³ of the gas phase of the cell was transferred to the Van Slyke and the gases were drawn into an evacuated sample cell with septum and stored at about 1500 mbar pressure. Knowing the solubilities of the various products one could readily include the amounts of dissolved gases in the calculation of the yields. These amounts were rather appreciable for acetylene and butadiene. Two separate conditions existed in the insonation experiments, which we call the turbulent and nonturbulent conditions. In the nonturbulent case there was only a gentle movement of the surface of the insonated liquid. In the turbulent case, violent movement of the liquid was observed. The power of the ultrasound was practically the same, just the position of the glass vessel in the ultrasonic field was slightly changed. The yield of H_2O_2 in the irradition of water under pure argon was practically the same in both cases. However, the gas exchange between the irradiated solution and the atmosphere above the solution was less extensive in the nonturbulent case. As a con-

(4) Fischer, Ch.-H.; Hart, E. J.; Henglein, A. J. Phys. Chem. 1986, 90, 222

sequence, gaseous reaction products did not rapidly escape the solution and were recycled into the bubble and further decomposed.

Results

Figure 1 shows how the concentration of various products increases with increasing insonation time. The decrease in D₂ and CH4 concentration is also shown. The solution was insonated under an atmosphere of 20 vol % CH₄, 40 vol % D₂, and 40 vol % Ar under nonturbulent conditions. As CH_4 is about twice as soluble in water as D_2 , the concentrations of the two reacting gases were about equal in the liquid phase. Among the products, HD and H₂ are the most prominent. All four deuteriated methanes were observed; CD₄ having a very low yield is not shown in the figure. While the yields of D_2 and CH_4 consumption and those of HD and H₂ do not change with time, those of the deuteriated methanes decrease at longer times. This indicates that the deuteriated methanes are consumed upon their accumulation in the solution.

In the experiments of Figure 2, solutions were insonated for 1 h under a gas atmosphere which contained a CH_4-D_2 (1:2) mixture and argon in various ratios. Overall rates were calculated by dividing the concentration changes after 60 min by the insonation time. As nonturbulent conditions were chosen, the rates for the deuteriated methanes are not true rates of formation but are lowered due to some decomposition of these products (see Figure 1). It is seen that all rates pass through a maximum which lies close to 60 vol % of the $CH_4 + D_2$ mixture. Only the maximum for H₂ appears at a much lower concentration, i.e. 20 vol %. The deuteriated methanes were also determined after a much shorter insonation time of 5 and 10 min and under turbulent conditions, i.e. under conditions where rapid equilibration with the gas phase took place. Figure 3 shows the initial rates of formation of these products.

In the experiments of Figure 4, the initial rates of formation of the more abundant deuteriated methanes are plotted as functions of the composition of the CH₄-D₂ mixture, the concentration of argon in the atmosphere always being 40 vol %. The maximum rate of formation is shifted to higher D₂ concentrations with increasing deuterium content of a product. At D₂:CH₄ ratios larger than about 5:1, CH_2D_2 is even more abundant than CH_3D .

The minor products were higher hydrocarbons and carbon monoxide. The rate of CO formation is also shown in Figure 2. It appeared only between 5 and 60% of the CH_4 -D₂ mixture. At concentrations lower than 10% small amounts of carbon dioxide could be detected. The yields of the hydrocarbons were much lower than those of the deuteriated methanes as can be seen from Figure 5. It should also be mentioned that the irradiated solutions were slightly turbid and that a very small amount of precipitate, possibly carbon, settled on the bottom of the irradiation vessel.

The hydrogen, H₂, in Figure 2 could have originated from water or methane molecules. In order to obtain some information about this question, the experiments of Figure 6 were carried out, in which water was insonated under an atmosphere of argon plus deuteriated methane, CD4. The rate of formation of the various isotopic forms of hydrogen is plotted as a function of the com-

⁽¹⁾ Henglein, A. Z. Naturforsch. B 1985, 40b, 100.

 ⁽²⁾ Hart, E. J.; Henglein, A. J. Phys. Chem. 1986, 90, 5992.
 (3) Hart, E. J.; Henglein, A. J. Phys. Chem. 1986, 90, 3061.

⁽⁵⁾ Fischer, Ch.-H.; Hart, E. J.; Henglein, A. J. Phys. Chem. 1986, 90, 3959

⁽⁶⁾ Fischer, Ch.-H.; Hart, E. J.; Henglein, A. J. Phys. Chem. 1986, 90 1954

⁽⁷⁾ Hart, E. J.; Fischer, Ch.-H.; Henglein, A. J. Phys. Chem. 1986, 90, 5989

⁽⁸⁾ Neppiras, E. A. Phys. Rep. 1980, 61, 159.



Figure 1. Concentration of various products and consumption of D_2 and CH_4 as functions of the insonation time.



Figure 2. Overall rates of formation of the products and of the disappearance of reactants as functions of the composition of the argon- CH_4-D_2 atmosphere. The ratio of the concentrations of $CH_4:D_2$ was always 1:2. The time of insonation was 60 min.

position of the gas atmosphere. The yield of H_2 , which stems from the decomposition of water molecules, rapidly increases with increasing CD₄ concentration and decreases again at concentrations greater than 10%. The yields of HD and D₂ also pass through maxima, which are positioned at higher concentrations of CD₄. The inset of Figure 6 shows the rate of consumption of CD₄ as well as the rates of formation of all isotopic hydrogen molecules, ΣH_2 , and of carbon monoxide.

Discussion

Overall Processes. All possible deuteriated methanes, i.e. CH_3D , CH_2D_2 , CHD_3 , and CD_4 , are formed upon the passage of ultrasound through an aqueous solution of methane, deuterium, and argon. Maximum yields are observed at 40 vol % argon in the gas mixture and at a ratio $D_2:CH_4$ of about 2. Under these conditions, the deuteriated methanes are the main products of the conversion of CH_4 . This can be recognized by comparing the sum of the yields in Figure 3, which amounts to 36 μ M·min⁻¹, with the yield of CH_4 disappearance in Figure 2 which is 40 μ M·min⁻¹. That relatively little methane is consumed to form other products



Figure 3. Initial rates of formation of deuteriated methanes at various compositions of the gas atmosphere. CH_4/D_2 ratio = 1:2. The time of insonation was 5 min.



Figure 4. Rates of formation of deuteriated methanes as functions of the composition of the CH_4-D_2 mixture. The concentration of argon was 40 vol %.

can also be recognized from the rates in Figure 5. We calculate from the data in this figure that methane disappears at 60 vol % CH₄ + H₂ with a rate of 14 μ M·min⁻¹ to form the hydrocarbons.

However, a third process must also take place besides deuterium exchange and condensation of methane. This is recognized by looking at the difference in the consumption of D_2 and the formation of the deuteriated products. At 60 vol % $CH_4 + D_2$, D_2 disappears at a rate of 70 μ M·min⁻¹, which corresponds to the disappearance of D atoms of 140 μ M·min⁻¹. On the other hand, one calculates that D atoms are used to form deuteriated methanes with a rate of 61 μ M·min⁻¹ (Figure 3). HD is produced at a rate of 43 μ M·min⁻¹. Thus, 140 - 61 - 43 = 36 μ M D atoms per minute which disappeared cannot be found in those products. It should be remembered that H-D isotopic exchange takes place in the insonation of water containing D₂, the products being HD and HDO.⁴ This isotopic exchange probably is the reason why 36 μ M·min⁻¹ D atoms are missing in the above material balance.



Figure 5. Rate of formation of the higher hydrocarbons as a function of the composition of the gas atmosphere.



Figure 6. Rate of formation of the various isotopic hydrogen molecules as a function of the composition of the argon-CD₄ atmosphere. Inset: rates of formation of CO and $\sum H_2$ (sum of all hydrogen molecules) and of the consumption of CD₄.

In the previous study it was found that H_2 is an important product of the isotopic exchange in the D_2 - H_2O system. In fact, one observed a strong increase in the yield upon adding small amounts of D_2 to the argon atmosphere.⁴ A similar observation was now made in the experiments of Figure 6 when the addition of small amounts of CD_4 also leads to a drastic increase in the H_2 yield. It thus seems probable that the large H_2 yield at 20 vol % $CH_4 + D_2$ in Figure 2 comes mainly from a decomposition of H_2O and to a lesser degree of CH_4 molecules in the argon cavitation bubbles.

Elementary Reactions. With respect to the formation of carbon monoxide, higher hydrocarbons, and small amounts of carbon, the sonolysis of methane in argon bubbles resembles the combustion of methane with an oxygen deficit. However, oxygen was not present in the sonolysis, water being the supplier of oxygen in this unusual combustion process.

Water, methane, and deuterium molecules were present in the cavitation bubbles, and all three molecules may be expected to be decomposed into free radicals or atoms. In the case of water it is known that the primary process of decomposition is

$$H_2O \rightarrow H + OH$$
 (1)

Both the H atoms and OH radicals have been detected by an ESR spin trap method.⁹ It is also known that a large part of these radicals recombine in the hot bubbles

$$H + OH \xrightarrow{M} H_2O$$
 (2)

and that OH radicals form O atoms⁶

$$2OH \rightleftharpoons O + H_2O \tag{3}$$

The participation of these radicals and atoms in the sonolytic reactions should be most pronounced at low concentrations of $CH_4 + D_2$ in the bubbles, i.e. at relatively large ratios of $[H_2O]/[CH_4 + D_2]$. The large increase in the H_2 yield in the presence of small amounts of methane or/and deuterium is attributed to the scavenging of oxidizing radicals and atoms by these additives:

$$OH + D_2 \rightarrow HDO + D$$
 (4)

$$OH + CH_4 \rightarrow H_2O + CH_3 \tag{5}$$

$$O + D_2 \xrightarrow{M} D_2 O \tag{6}$$

$$O + CH_4 \rightarrow H_2O + CH_2 \tag{7}$$

$$CH_2 + O \rightarrow CO + 2H$$
 (8)

The H atoms from the decomposition of water molecules thus escape recombination with the oxidizing radicals and form more H₂. The formation of CO is explained by reaction 8 which is well-known from combustion chemistry.¹⁰ At low concentrations of D₂ and CH₄, CO molecules can further be attacked by oxidizing radicals which explains the formation of CO₂. At the higher concentrations of D₂ and CH₄, the H atoms are more efficiently scavenged, such as

$$H + D_2 \rightarrow HD + D \tag{9}$$

and reactions of the fragments of methane will become more important.

$$CH_4 \rightarrow CH_3 + H$$
 (10)

$$CH_4 \rightarrow CH_2 + H_2$$
 (11)

$$CH_3 + D_2 \rightarrow CH_3D + D$$
 (12)

$$CH_2 + D_2 \xrightarrow{M} CH_2D_2$$
 (13)

This explains why the H_2 yield decreases and the yields of HD and the deuteriated methanes increase at higher concentrations of CH_4 - D_2 . That these yields also pass through maxima is understood in terms of the lower temperatures which exist in the cavitation bubbles as both CH_4 and D_2 have lower ratios of the specific heats than argon.

We have listed only reactions 10 and 11 as important processes in the pyrolysis of methane. In conventional combustion studies, reaction 11 is regarded as of little importance.¹¹ However, the transient temperatures of 3000–4000 °C in the cavitation bubbles⁷ are so high that extraordinary processes of methane decomposition may occur. It is even conceivable that decompositions of the type

$$CH_4 \rightarrow CH + H + H_2$$
 (14)

$$CH_4 \rightarrow C + 2H_2 \tag{15}$$

occur. These reactions explain the formation of carbon and of the highly deuteriated methanes, CD_4 and CHD_3 . Another process that could lead to these deuteriated products is the consecutive fragmentation and deuteriation of methane molecules, such as the reaction of CH_2D_2 resulting from reaction 13

$$CH_2D_2 \rightarrow CHD_2 + D$$
 (16)

 ⁽⁹⁾ Makino, K.; Mossoba, M. M.; Riesz, P. J. Phys. Chem. 1983, 87, 1369.
 (10) Warnatz, J. In Combustion Chemistry, Gardiner, W. C., Ed.;
 Springer-Verlag: West Berlin, 1984; Chapter 5.

⁽¹¹⁾ Warnatz, J. Ber. Bunsen-Ges. Phys. Chem. 1983, 87, 1008.

$$CHD_2 + D_2 \rightarrow CHD_3 + D \tag{17}$$

These consecutive reactions take place in the same cavitation event.

Among the higher hydrocarbons, acetylene is the major product at medium concentrations of $CH_4 + H_2$ (Figure 5). However, at higher concentrations the yields of ethane and ethylene are greater. This effect indicates lower temperatures in the cavitation bubbles when much $CH_4 + H_2$ is present.

At the present time it is difficult to give a more detailed mechanism for the reactions observed. With respect to the deuterium exchange it would be interesting to study the pyrolysis of mixtures of CH_4 and D_2 and to make a comparison with the data obtained in sonolysis. Our present findings again show that very drastic temperature conditions exist in the cavitation bubbles which act as microsystems for the pyrolysis of gases surrounded by a cold water bath in which many products of pyrolysis are rapidly cooled and stabilized.

Registry No. CH₄, 74-82-8; D₂, 7782-39-0; H₂, 1333-74-0; H₂O, 7732-18-5.

Pressure Effects on Dielectric Relaxation of Supercooled o-Terphenyl

Motosuke Naoki,* Hideki Endou, and Katsuhiro Matsumoto

Department of Textiles and Polymers, Faculty of Technology, Gunma University, Kiryu, Gunma 376, Japan (Received: October 24, 1986)

The dielectric relaxation time in the supercooled liquid state of o-terphenyl has been obtained as a function of temperature and pressure. The enthalpy of activation, H^* , and its temperature variation coincide with those for viscous flow. The internal energy of activation defined by $E^* = H^* - PV^*$ at each pressure, where V^* is the volume of activation, is superposable along pressure, and the mechanism for the relaxation process may be scarcely altered by pressure. This is supported by the fact that the Williams-Watts distribution parameter is scarcely altered by the pressure. The energy of activation at constant volume, E^*_{V} , is almost the same as the energy required to form the volume of activation inside the liquid. The value of E^* for o-terphenyl is much smaller than those for polymers in the supercooled liquid region. The nature of the relaxation processes for some different types of liquids may be classified by the quantity E^*_V/H^* or P_iV^*/E^* .

Introduction

Since o-terphenyl can readily be vitrified and its glass transition temperature is relatively high, there have been presented various investigations¹⁻⁸ and discussions⁹⁻¹¹ on molecular mobility in the o-terphenyl liquid. In previous papers,¹²⁻¹⁴ we investigated the molecular mobility in the supercooled liquid of a mixture of triphenylchloromethane and o-terphenyl from studies on the pressure dependences of the thermodynamic properties and the dielectric relaxation process. The mixture was employed because of its suitably high dielectric constant and the very stable supercooled liquid state. However, the mixture is easy to handle, but much too complicated to analyze the mobility of each component. For simplicity, a pure component liquid may be more desirable for this subject. The repeated recrystallizations of oterphenyl from methyl alcohol makes the supercooled liquid state more stable and the sample recrystallized five times has been found to be stable enough in our pressure dielectric cell. In this paper, we report the variations of the dielectric relaxation time with

(1) Andrews, J. N.; Ubbelohde, A. R. Proc. R. Soc. London, Ser. A 1955, 228, 435.

temperature and pressure and some activation parameters are discussed. The results are compared with those on the pressure variation of dynamic light scattering obtained by Fytas et al.,⁸ on the wide ranged temperature variations for viscous flow,¹⁻⁵ and on the activation parameters for poly(vinyl chloride).

Experimental Section

The supercooled liquid state of the o-terphenyl sample, purchased from Tokyo Chemical Industry Co., was stable in the Pyrex glass tube, but not in the pressure dielectric cell made of stainless steel and teflon, i.e., the commercial o-terphenyl usually crystallized in a few hours at room temperature. The supercooled liquid melted from the crystallites, prepared by repeating recrystallizations five times from methyl alcohol and dried under vacuum for several weeks, is stable for over a week in the dielectric cell. The liquid sample thus prepared was loaded at 70 °C into the pressure dielectric cell, the details of which are shown elsewhere.12

The dielectric constants were measured by a General Radio 1620-A capacitance measuring assembly, in conjunction with a General Radio 1310-B oscillator employed to make small changes in frequency near the dielectric loss peaks. The correction for stray capacitance was made by measuring the dielectric constant of benzene (Uvasol grade, Merck).¹⁵ However, the cell constant under elevated pressures was not determined and the present dielectric data are given by the reduced dielectric loss, $\epsilon^{\prime\prime}/\epsilon^{\prime\prime}{}_{\rm max},$ where ϵ''_{max} is the maximum value of the dielectric loss at a given temperature and pressure.

The experimental procedure was as follows. The dielectric cell was set in the pressure vessel which had been preheated to about 80 °C. Then the vessel was cooled to the lowest temperature of each experiment at atmospheric pressure, and the pressure was raised to the pressure intended, e.g., 0.1, 19.6, 39.2, 58.8, or 78.5 MPa. The temperature was raised in small steps (ca. 1 °C) and

⁽²⁾ McLaughlin, E.; Ubbelohde, A. R. Trans. Faraday Soc. 1958, 54, 1804.

⁽³⁾ Greet, R. J.; Turnbull, D. J. Chem. Phys. 1967, 46, 1243.

 ⁽⁴⁾ Laughlin, W. T.; Uhlmann, D. R. J. Phys. Chem. 1972, 76, 2317.
 (5) Cukierman, M.; Lane, J. W.; Uhlmann, D. R. J. Chem. Phys. 1973, 59, 3639.

⁽⁶⁾ McCall, D. W.; Douglass, D. C.; Falcone, D. R. J. Chem. Phys. 1969, 50, 3839.

⁽⁷⁾ Fytas, G.; Wang, C. H.; Lilge, H.; Dorfmuller, Th. J. Chem. Phys. 1981, 75, 4247.

⁽⁸⁾ Fytas, G.; Dorfmuller, Th.; Wang, C. H. J. Phys. Chem. 1983, 87, 5041

 ⁽⁹⁾ Greet, R. J.; Turnbull, D. J. Chem. Phys. 1967, 46, 1243.
 (10) Chang, S. S.; Bestul, A. B. J. Chem. Phys. 1972, 56, 503.

⁽¹⁰⁾ Chang, S. S., Bestul, A. B. J. Chem. Phys. 197, 56, 505.
(11) Atake, T.; Angell, C. A. J. Phys. Chem. 1979, 83, 3218.
(12) Naoki, M.; Matsushita, M. Bull. Chem. Soc. Jpn. 1983, 56, 2396.
(13) Naoki, M.; Matsushita, M. Bull. Chem. Soc. Jpn. 1983, 56, 3549.
(14) Naoki, M.; Matsumoto, K.; Matsushita, M. J. Phys. Chem. 1986, 90, 4423.

⁽¹⁵⁾ Vij, J. K.; Scaife, W. G. S. J. Chem. Phys. 1976, 64, 2226.