an increasing energy separation of levels—a consequence of the positive anharmonicity. This is particularly evident in the ground state with the relatively broad minimum of the ground-state potential.

One motivation behind the present work has been the pursuit of accurate spatially resolved temperatures of flames based on sequence structure peak areas. Franck–Condon factors for the sequence structure were generated from the normalized coefficients used in the diagonalization procedure and scaled with room temperature Boltzmann factors. These total combined factors along with their associated Franck–Condon factors are given in Table II and demonstrate the good agreement between the theoretical and experimentally acquired peak areas. This agreement indicates little contribution of kinetic terms such as geometric saturation or ac stark shifts to the overall dependences of the peak areas and demonstrates the feasibility of nonintrusively determining spatially resolved temperatures.

Sequence structure similar to that of the A ← X transition has also been observed in the hot-band region of the B ← X[9,10] state. Analysis of the spectra in Figure 5 of ref 9 (one-photon absorption around 260 nm) yielded the same ground-state potential as the present study and, within experimental uncertainty, a similar excited-state potential as that of the A state. This suggests a minor deviation in the influence of the B state's electronic manifold (composed of nitrogen's $3p_{x,y}(+)$ orbitals) over the A state's manifold (composed of nitrogen's 3s(+) orbitals) on the torsional vibration.

Conclusion

Franck–Condon factors and energy positions for a number of levels of the ν_{13} torsional mode have been determined for the A ← X transition of Dabco. This data has been shown useful in measuring vibrational levels over a wide temperature range in difficult environments. The technique is simple and ions, as in the present study, or fluorescence (centered around 300 nm)[14] can be monitored with gated electronics. Further work on preheating and pyrolysis of Dabco in atmospheric and low-pressure flames is now in progress.

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H/D Isotope Exchange in the D_2–H_2O System under the Influence of Ultrasound

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Water was irradiated by 300-kHz ultrasound under atmospheres of argon, deuterium, and mixtures of the two gases, and the isotopic composition of the gas was determined. The yields of H_2 and HD increase with increasing deuterium content of the gas mixture, reach maxima at 35% D_2 (H_2) and 60% D_2 (HD), and fall off at higher D_2 concentrations. The yield of the D_2 consumption peaks at 50% D_2. The absolute yields are greater by almost one order of magnitude than those of ordinary sonolytic reactions such as H_2O_2 formation. The results are explained by reactions of the H and OH radicals generated in the sonolysis of water. In the absence of deuterium, a large percentage of these radicals recombine. D_2 at low concentrations scavenges mainly OH radicals, the principal products being H_2 and HDO. At higher D_2 concentration, D_2 also scavenges H atoms, the principal products now being HD and HDO. The decrease in all yields at higher D_2 concentrations is explained by the lower temperatures reached in the gas bubbles, which are formed by cavitation.

Introduction

The chemical effects of ultrasonic waves in aqueous solutions are brought about by the high temperatures and pressures which exist for a short time during the nearly adiabatic compression phase of oscillating or collapsing gas bubbles.[1] When water is irradiated under argon, H_2 and H_2O_2 are generated and a smaller amount of O_2 is formed. Dissolved substances often are oxidized or reduced, the yields generally being of the same order of magnitude as that of the H_2O_2 formation in pure water.[2] The initial step of the sonolysis of water is the thermal dissociation

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

Both H and OH recently were detected in ESR spin-trapping experiments.[3] H_2 and H_2O_2 are formed via the combination of radicals. It was previously shown that the yields of some chemical reactions are substantially increased when gaseous radical scavengers such as oxygen or methane are present in moderate concentrations in an argon atmosphere.[4-6] In the present work, deuterium was used as a scavenger, and the D–H exchange between D_2 and H_2O was investigated by measuring the isotopic composition of the gas after irradiation. In these experiments, water was irradiated under various mixtures of argon and deuterium. At D_2 contents greater than 10%, H_2O_2 was no longer a product, i.e. in most of these experiments H–D exchange was the only process occurring.

The D_2–H_2O exchange reaction under the influence of γ-rays has previously been reported.[7] It was found to be initiated by the free radicals from the radiolysis of water. It is known from a number of studies that the reactions in sonolysis occur to a large extent in the gaseous phase. This has also to be taken into consideration in discussing the sonolytically initiated exchange reaction.

Experimental Section

Water was deaerated by evacuation with a diffusion pump. Deaerated water (100 mL) was saturated with the desired D_2–Ar mixture. The glass irradiation vessel had a volume of 66.5 cm^3 and could be closed during irradiation. It was completely filled with the D_2–Ar solution displacing the argon used to purge the vessel. Finally, 15 cm^3 of solution was displaced by the gas mixture. By this procedure, 51.5 cm^3 of H_2O was in the vessel

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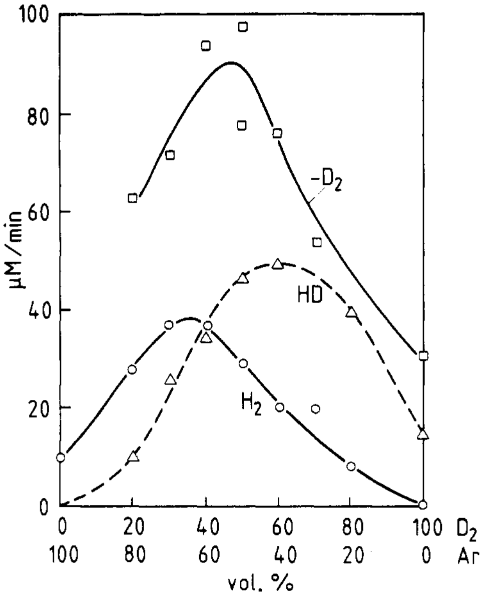

Figure 1. Rates of formation of H_2 and HD and of the consumption of D_2 in the ultrasonic irradiation of water under various mixtures of argon and deuterium.

with 15-cm^3 gas phase. After irradiation, 15 cm^3 of water was added to the solution and the gas pushed into a syringe. The gas finally was injected into a mass spectrometer for isotopic analysis. All these procedures were made using standard Van Slyke and syringe techniques.[8] Much care was taken to make sure that no traces of air were present during irradiation and analysis.

The ultrasound was delivered by the 300-kHz quartz generator previously described.[6] The power dissipation in the liquid was 12 W as determined from the rise in temperature in an experiment without a cooling water bath. During the irradiation the increase in temperature was less than 1 °C.

Results

The rates of formation of HD and D_2 and that of the consumption of D_2 are plotted in Figure 1 as functions of the composition of the argon–deuterium mixture. The conversion of D_2 was between 5 and 15% in these experiments. The rate of D_2 consumption had therefore to be calculated as the difference in two large numbers. This explains the rather large scattering of the data for $-D_2$ in Figure 1. Under pure argon, the rate of H_2 formation was 10 μM min^{-1}. H_2O_2 was formed at a rate of 8.0 μM min^{-1} under these conditions, the difference in oxidation equivalents between the two yields being due to O_2 formation. The addition of D_2 caused the H_2 yield to increase. The O_2 and H_2O_2 yields (not shown in the figure) rapidly decreased to practically zero at 10% D_2. A maximum yield of 37 μM min^{-1} for H_2 was observed at 35% D_2 in the gas mixture. Under pure D_2, no H_2 was found.

The HD yield increased in a somewhat different way, a maximum yield of 49 μM min^{-1} being attained at 60% D_2. A noticeable HD yield was still observed under pure D_2. The rate of decrease in D_2 concentration also went through a maximum (at 50% D_2). The rate of D_2 consumption was much greater than that of HD formation. We conclude that most of the D atoms consumed appeared in the form of HDO in the liquid. No experiments were undertaken to trace HDO as there are no other deuterium-containing products besides HD and HDO. Note that the rate of D_2 consumption at the maximum (90 μM min^{-1}) is about ten times greater than that of a more usual sonochemical reaction such as H_2O_2 formation.

Two overall processes for isotopic exchange between deuterium and water may be written:

$$D_2 + H_2O \rightarrow HD + HDO \qquad (2)$$

$$D_2 + 2H_2O \rightarrow H_2 + 2HDO \qquad (3)$$

As all three products, i.e. H_2, HD, and HDO, appear, one has to postulate that both processes, 2 and 3, occur in the ultrasonic irradiation of water under an argon–deuterium atmosphere. In mixtures with comparable percentages of the two gases, processes 2 and 3 are roughly equal. In the irradiation under pure D_2, where H_2 is not formed, only exchange process 2 takes place.

Discussion

The maximum yields for H_2 and HD formation and D_2 consumption are much higher than the yields of H_2 and H_2O_2 observed in the irradiation of water under pure argon. This effect is understood in terms of the radical recombination reaction

$$H + OH \xrightarrow{M} H_2O \qquad (4)$$

which occurs very efficiently in the absence of a gaseous scavenger.[5,6] In the presence of sufficient D_2, all the primary H and OH radicals are scavenged to form the final products of HD exchange with large yields:

$$OH + D_2 \rightarrow OHD + D \qquad (5)$$

$$H + D_2 \rightarrow HD + D \qquad (6)$$

$$H + H \xrightarrow{M} H_2 \qquad (7)$$

$$H + D \xrightarrow{M} HD \qquad (8)$$

At low D_2 concentrations, mainly OH radicals are scavenged (eq 5), the remaining H atoms forming H_2 and HD (eq 7 and 8). With increasing D_2 concentration, reaction 6 also becomes important, the result being that the HD yield becomes more important than that of H_2 at moderate D_2 concentrations. These considerations explain why the maximum of the curve for HD in Figure 1 appears at a higher D_2 concentration than the maximum of the curve for H_2. Finally, when the D_2 concentration in the gas mixture becomes too high, a lower temperature is reached in the nearly adiabatic compression phase of the gas bubbles. This effect finally leads to a decrease in all yields in Figure 1 at the higher D_2 concentrations.

A rough estimate of the radicals that recombine (eq 4) may be made. The maximum H_2 yield at 35% D_2 in Figure 1 is about four times greater than the H_2 yield in the irradiation under pure argon, and the HD yield at 35% D_2 is about twice the yield of H_2 in the absence of D_2. We assume that the yield of the primary decomposition reaction (eq 1) is not yet significantly decreased at 35% D_2. It can then be derived from the above mechanism that about 80% of the radicals generated initially recombine in the absence of D_2. This corroborates our previous conclusions about the importance of the recombination reaction.[5,6]

We must still discuss another thermal decomposition reaction which may take place in the presence of D_2. Since the bond strength in D–D is lower than that in H–OH, it seems plausible that deuterium molecules also are dissociated in the gas bubbles:

$$D_2 \rightarrow 2D \qquad (9)$$

In fact, it is known that the reducing effects of ultrasound are strongly enhanced in the presence of hydrogen in the argon atmosphere.[9] The D atoms formed contribute to the isotopic exchange by reacting with water molecules according to

$$D + H_2O \rightarrow HD + OH \qquad (10)$$

This reaction is endothermic by only 0.6 eV, and it cannot be excluded that part of the HD results from it. However, the reasons may be mentioned for reaction 10 not being of great importance. In the first place, the formation of H_2 cannot be explained in this way. Secondly, HD should be formed in a very large yield as the chain reaction of eq 10 and 5 becomes possible. The yield of HD, however, did not substantially exceed that of H_2, i.e. the yield of

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a product which did not stem from a chain reaction.

We conclude that the isotope exchange between D_2 and H_2O can be explained by free-radical reactions on the basis of principles which have been derived previously in studies on other chemical reactions. These principles include the dissociation of H_2O in the collapsing gas bubble, the recombination reaction of radicals in the absence of a gaseous scavenger, and the dependence of these yields on the composition of the argon–D_2 gas atmosphere under which water is sonolyzed.

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