served in all three studies; the agreement between this work and Walker's results is striking. In addition, we find that our rate coefficients per primary C-H bond for H-atom abstraction by OH from ethane, propane, and neopentane are nearly identical at about T = 690 K. It would thus appear that Walker's primary H-atom reaction standard, OH + neopentane at 753 K, is well chosen.

The kinetic isotope effect for H- or D-atom abstraction from a secondary reaction site in propane may also be determined from the $k_{\rm H}^{\rm S}(T)$ and $k_{\rm D}^{\rm S}(T)$ results compiled in Table IV. As detailed in our earlier papers,^{1,2} it is instructive to represent the kinetic isotope effect by a two-parameter expression of the form $k_{\rm H}{}^{\rm S}$ $k_{\rm D}^{\rm S}(T) = I \exp(C/RT)$. Best-fit values of I and C and their associated $\pm 2\sigma$ uncertainties are 1.13 \pm 0.19 and 521 \pm 155 cal mol⁻¹, respectively. This result is plotted, along with the $k_{\rm H}^{\rm S}$ / $k_{\rm D}^{\rm S}(T)$ results, in Figure 4. These values of I and C are significantly different from those that characterize the primary kinetic isotope effects found in OH + ethane and OH + neopentane. They are, however, very similar to those found in studies of the reactions between OH and cyclopentane or cyclohexane,³³ two

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alkanes that contain only secondary C-H abstraction sites. Theoretical analyses of these results are in progress.

Summary

We have accurately determined rate coefficients for H- and D-atom abstraction by OH from six selectively deuterated isotopes of propane. Consistent with our results on the OH + ethane reaction, we find that the reactivity of individual methyl or methylene groups in propane is independent of the hydrogen isotopic content of the remainder of the molecule. From our measurements, we have determined the temperature-dependent branching ratios for the formation of *n*-propyl and isopropyl radicals in the reaction between C3H8 and OH and have characterized the kinetic isotope effect for secondary H- and D-atom abstraction by OH in propane.

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Ultrasonic Irradiation of Water in the Presence of ^{18,18}O₂: Isotope Exchange and Isotopic Distribution of H₂O₂

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Water was irradiated by 300-kHz ultrasound under argon, oxygen-18, and mixtures of these two gases, and the isotopic distribution of O_2 and H_2O_2 was determined. The consumption of ${}^{18,18}O_2$ was much faster than the formation of H_2O_2 . All possible isotopic O_2 and H_2O_2 molecules were found, the ${}^{16}O$ -containing products being most abundant. Isotopic exchange and H_2O_2 formation occur through common intermediates. A mechanism is proposed in which radical reactions in hot gas bubbles occur as in combustion chemistry and in which the isotopic identity of the radicals and atoms originally produced from ${}^{16}OH_2$ and ${}^{18,18}O_2$ is partly lost. The final products O_2 and H_2O_2 are postulated to be formed in a cooler interfacial region.

Introduction

Hydrogen peroxide is known to be formed when ultrasonic waves at intensities sufficient to produce cavitation are propagated through water.^{1,2} The liquid has to contain a monoatomic gas, such as argon, or a diatomic one, such as oxygen. When water saturated with a 70:30 argon-oxygen mixture is irradiated, drastically higher yields of H_2O_2 are produced than with the pure gases.^{3,4} H atoms, OH radicals, O atoms, and HO₂ radicals are believed to be the intermediates.

Although isotopic techniques have first been applied in radiolysis to study radical reactions in aqueous solution,⁵ isotope techniques in sonolysis were first used by Del Duca et al. to study the mechanism of H_2O_2 formation.⁶ They irradiated water under ¹⁸O-enriched oxygen and reported that two-thirds of the H_2O_2 produced originated from the oxygen gas. It was also concluded that the O-O bond was not broken. These results indicated that the primary step was the dissociation of water

$$H_2 O \rightarrow H + {}^{16}OH \tag{1}$$

and that hydrogen peroxide was formed via the free-radical reactions

$${}^{16}\text{OH} + {}^{16}\text{OH} \rightarrow {}^{16,16}\text{O}_2\text{H}_2$$
 (2)

$$H + {}^{18,18}O_2 \rightarrow {}^{18,18}O_2H$$
 (3)

$${}^{18,18}O_2H + {}^{18,18}O_2H \rightarrow {}^{18,18}O_2H_2 + {}^{18,18}O_2$$
 (4)

However, the experimental conditions in this study were rather poor owing to the fact that oxygen with only 1.4% enrichment in ¹⁸O was used.

The next isotopic study was made by Anbar and Pecht.⁷ They irradiated solutions of ${}^{16,16}O_2$ in ${}^{18}OH_2$ and ${}^{18,18}O_2$ in ${}^{16}OH_2$ and found comparable amounts of ${}^{16,18}O_2H_2$ and ${}^{18,18}O_2H_2$ in both cases. The formation of the isotopically mixed hydrogen peroxide was explained by the generation of oxgyen atoms via dissociation of O_2 and reactions of the O atoms with water:

$$O + H_2 O \rightarrow H_2 O_2 \tag{5}$$

This reaction can occur only when the oxygen atom is in the first excited singlet state. The formation of ground-state oxygen atoms by thermal dissociation of O_2 in the cavitation bubbles has recently

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Figure 1. Rate of formation of various products and of $^{18,18}O_2$ consumption as functions of the $^{18,18}O_2$ concentration in the argon-oxygen-18 mixture under which water was irradiated.

been suggested to explain the yields of certain redox reactions, such as the oxidation of iodide.⁴

In the present paper, the results of a more elaborate investigation of the isotope effects, which occur in the irradiation of oxygenated water, are reported. ¹⁶OH, was irradiated under argon, oxygen-18, and mixtures of these two gases. The isotopic composition of both the hydrogen peroxide formed and the oxygen gas after irradiation was determined. The results are more comprehensive than those obtained in the former studies, and they show that the mechanism is more complex than described by eq 1-5. An important fact which has not yet been considered in the earlier studies is that the radicals are generated in a region of extremely high temperature (in the compressed gas bubbles produced by cavitation) where they can hardly form stable molecules. The final products are formed when the radicals come into a cooler interfacial region. Before this happens the hot radicals may undergo various reactions in which their original isotopic identity is lost. These reactions occur under conditions similar to those in combustions. We therefore make use of known radical reactions in flames to explain our observed effects.

Experimental Section

The irradiation vessel could be connected to a Van Slyke apparatus which allows one to handle small amounts of gas. As described in a preceding paper on the H/D exchange in the irradiation of water under D₂, 51.5 mL of water was irradiated under 15 mL of gas, the vessel being closed during irradiation. By the procedure described, a sample of the gas was taken out after irradiation and analyzed in a mass spectrometer. The isotopic composition of the hydrogen peroxide formed was investigated by adding Ce(IV) to the solution and determining the isotopic composition of the oxygen evolved. The total amount of H₂O₂ was determined by adding iodide and ammonium molybdate to the irradiated solution and spectrophotometrically measuring the amount of I₂ formed.

Results

Figure 1a shows a plot of the yields of the various isotopic O_2 molecules as a function of the concentration of ^{18,18} O_2 in the argon-oxygen-18 mixture under which water was irradiated. The ^{18,18} O_2 consumption yield is also included. Figure 1b shows the yields of the isotopic H_2O_2 molecules. All yields pass through maxima, the maxima for H_2O_2 formation lying below and the maxima for isotopic O_2 formation and ^{18,18} O_2 consumption above 50% ^{18,18} O_2 in the gas mixture. Maxima in the yield vs. concentration curves have been reported previously for a number of chemical reactions which were initiated in aqueous solutions under mixtures of argon with another gas.^{3,4,8,9}

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Most striking is the high yield of ${}^{16,16}O_2H_2$ and the very low yield of ${}^{18,18}O_2H_2$. From the mechanism of Del Duca et al. (eq 1-4) one would expect a much higher yield of ${}^{18,18}O_2H_2$. The yield of ${}^{16,18}O_2H_2$ was always between those of the homoisotopic H_2O_2 molecules. Among the O_2 molecules, ${}^{16,16}O_2$ was found more frequently than ${}^{16,18}O_2$ at low ${}^{18,18}O_2$ concentrations in the gas mixture. However, at the higher ${}^{18,18}O_2$ concentrations the isotopically mixed molecule, ${}^{16,18}O_2$, was formed with the higher rate.

These results show that the following overall processes take place:

$$^{18,18}O_2 + 2^{16}OH_2 \rightarrow {}^{16,16}O_2H_2 + {}^{18,18}O_2H_2$$
 (6)

$$\rightarrow {}^{16,18}\text{O}_2\text{H}_2 + {}^{16,18}\text{O}_2\text{H}_2 \tag{7}$$

$$\rightarrow {}^{16,18}\text{O}_2 + {}^{18}\text{OH}_2 + {}^{16}\text{OH}_2 \tag{8}$$

$$\rightarrow {}^{16,16}\text{O}_2 + {}^{18}\text{OH}_2 + {}^{18}\text{OH}_2$$
 (9)

If reactions 6 and 7 for H_2O_2 formation occurred independently from reactions 8 and 9 for isotopic exchange, one would expect equal yields of ${}^{16,16}O_2H_2$ and ${}^{18,18}O_2H_2$. As this is not the case, we conclude that hydrogen peroxide formation and isotopic exchange are interconnected; i.e., there must be common intermediates.

Discussion

The increase in yield with increasing concentration of a gas added to the argon atmosphere is explained by the scavenging of H and OH radicals (eq 1).^{3,4,8} In the absence of the gaseous radical scavenger, about 80% of the radicals originally formed recombine:⁹

$$H + OH \rightarrow H_2O$$
 (10)

With increasing concentration of added gas, more and more radicals are scavenged. However, at higher concentrations of O_2 , a lower temperature is reached in the nearly adiabatic compression phase of the oscillating or collapsing gas bubbles. Oxygen has a lower value of γ (ratio of specific heats) than argon; i.e., the temperature is expected to decrease with increasing O_2 concentration in the gas mixture. These two opposing effects of the added gas produce the maximum in the yield vs. concentration curve.

^{16,16}O₂H₂ is formed in the combination of two ¹⁶OH radicals (eq 2). Figure 1b shows that 20% of ^{18,18}O₂ in the gas atmosphere increased the yield of ^{16,16}O₂H₂ by a factor of 4 as compared to the ^{16,16}O₂H₂ yield under pure argon. Many more ¹⁶OH radicals must have been formed in the presence of ^{18,18}O₂. This may in part be the result of the scavenging of H atoms by ^{18,18}O₂ (eq 3) as the recombination H + OH \rightarrow H₂O takes place to a lesser degree. However, the radical ^{18,18}O₂H formed in this way can be deactivated by reacting with an ¹⁶OH radical

$${}^{18,18}O_2H + {}^{16}OH \rightarrow {}^{16}OH_2 + {}^{18,18}O_2$$
 (11)

i.e., the H atom scavenging action of $^{18,18}O_2$ is not a satisfactory explanation for the increased production of ^{16}OH radicals.

Reactions 2 and 3 deserve a more critical consideration. Reaction 2 can occur only when the OH radicals encounter each other in solution. However, it is generally believed that the radicals are formed in the interior of extremely hot gas bubbles, where H_2O_2 is not stable. Reaction 2 cannot occur before the radicals have reached the cooler interfacial region between the hot gas phase and the bulk solution at ambient temperature. This interfacial region probably is not a thin interface consisting of one or two molecular layers of solvent molecules but is more voluminous. Across this region gradients in temperature and local radical concentration exist. Experiments with dissolved OH scavengers have recently led us to postulate that the OH radicals combine in this interfacial region.^{9,10} Before the radicals are

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cooled down they may undergo reactions as they are known from the chemistry of flames.¹¹ Instead of forming stable H_2O_2 , OH radicals disproportionate under these conditions

$${}^{16}\text{OH} + {}^{16}\text{OH} \rightarrow {}^{16}\text{OH}_2$$
 (12)

This reaction is exothermic by 0.6 eV. The reverse reaction

$${}^{16}\text{O} + {}^{16}\text{OH}_{2} \rightarrow {}^{16}\text{OH} + {}^{16}\text{OH}$$
 (13)

may readily occur at the temperatures of several thousand kelvin which exist in the compressed gas bubbles. In other words, hydroxyl radicals and oxygen atoms may be interconvertible in the hot gas. H_2O_2 is formed by OH radicals after cooling down, and the O atoms then combine to form O_2 :

$$O + O \to O_2 \tag{14}$$

Reactions 1, 12 and 14 explain the recent experimental result that a small amount of O_2 is formed (besides H_2 and H_2O_2) in the sonolysis of water under argon.^{4,12}

Let us now discuss the consequences of the occurrence of reactions 12–14 with respect to the isotopic distributions in the irradiated ${}^{18,18}O_2{}^{-16}OH_2$ system. As previously shown, O_2 molecules are thermally dissociated in hot gas bubbles; i.e., ${}^{18}O$ atoms are formed besides the dissociation products H and ${}^{16}OH$ of water:

$$^{18,18}O_2 \rightarrow ^{18}O + ^{18}O$$
 (15)

Reaction of an 18 O atom leads to an additional 16 OH radical and an 18 OH radical:

$$^{18}O + ^{16}OH_2 \rightarrow ^{18}OH + ^{16}OH$$
 (13a)

The combination of these radicals after cooling yields ${}^{16,16}O_2H_2$, ${}^{16,18}O_2H_2$, and ${}^{18,18}O_2H_2$. The conversion of ${}^{18}O$ atoms into ${}^{18}OH_2$ is possible via reaction 13a and

$${}^{18}\text{OH} + {}^{16}\text{OH} \rightarrow {}^{18}\text{OH}_2 + {}^{16}\text{O}$$
 (12a)

If the cycle of reactions 13a and 12a occurs a few times before

cooling down, a very large percentage of the ¹⁸O atoms will be found in the form of ¹⁸OH₂. This explains why ^{16,16}O₂ and ^{16,16}O₂H₂ are the main isotopic products in Figure 1a,b at low ^{18,18}O₂ concentrations. At the higher ^{18,18}O₂ concentrations, the isotopically mixed products ^{18,16}O₂H₂ and ^{18,16}O₂ are relatively more abundant. We explain this effect in terms of lower temperatures in the gas bubbles. Under these conditions, the cycle of reactions 12a and 13a occurs less efficiently; i.e., more ¹⁸O atoms and ¹⁸OH radicals keep their isotopic identity until they are cooled.

The occurrence of reaction 3 in the hot gas bubbles is highly improbable as H atoms react with O_2 at higher temperature according to

$$H + {}^{18,18}O_2 \rightarrow {}^{18}OH + {}^{18}O$$
 (16)

The ¹⁸OH radicals and ¹⁸O atoms may then react according to eq 12a and 13a and in this way produce additional ¹⁶OH and ¹⁶O species. These reactions explain why small amounts of ^{18,18}O₂H₂ are formed and why the ¹⁶O-labeled products are so abundant.

We conclude that HO_2 radicals form only in low yield when oxygenated water is irradiated by ultrasound and then probably only in the cooler interfacial region. However, it was recently reported that the anion of this radical, O_2^- , is formed with a relatively long lifetime and in appreciable yield when strongly alkaline solutions are irradiated.⁴ It seems conceivable that HO_2 radicals are produced via the reaction

$$OH + H_2O_2 \rightarrow H_2O + HO_2$$
(17)

in the liquid interfacial region where the local concentration of H_2O_2 is high.

In conclusion, we stress that the isotopic effects in the system $^{18,18}O_2$ - $^{16}OH_2$ can be explained by H, OH, and free O atom reactions. The chemistry occurring is mainly composed of radical reactions in the hot gas phase and in the cooler interfacial region. A few radicals escape into the bulk solution.⁴ The results from radiation chemistry and combustion chemistry help formulate the reactions of radicals in sonolysis.

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Registry No. H₂O, 7732-18-5; ¹⁸O₂, 14797-71-8.

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