Isotope effect in the formation of hydrogen peroxide by the sonolysis of light and heavy water

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The kinetics of the formation of hydrogen peroxide by the sonolysis of light and heavy water in argon and oxygen atmospheres was investigated. The sonochemical reaction has a zero order with respect to hydrogen peroxide (H_2O_2, D_2O_2, or DHO_2). The measurement of the kinetic isotope effect (α), defined as the ratio of the reaction rates in H_2O and D_2O, carried out under argon gave a value of 2.2±0.3. The observed isotope effect decreases with an increase in the concentration of light water in H_2O—D_2O mixtures. No isotope effect is displayed in the oxygen atmosphere (α = 1.05±0.10). The isotope effect is determined presumably by the mechanism of sonochemical decomposition of water molecules, which includes the H_2O—Ar^* and D_2O—Ar^* energy exchange (where Ar^* are argon atoms in the $^3P_{2,0}$ excited state) in the nonequilibrium plasma generated by a shock wave, arising upon a cavitation collapse.

Key words: ultrasound, isotope effects, heavy water.

Study of the formation of hydrogen peroxide generated on ultrasonic treatment of water has shown[1—5] that the mechanism of water sonolysis in an inert gas includes dissociation of H_2O molecules inside a cavitation bubble and subsequent recombination of $H^{\cdot}$ atoms and $OH^{\cdot}$ radicals

$$H_2O \longrightarrow H^{\cdot} + OH^{\cdot}, \tag{1}$$

$$2\,H^{\cdot} \longrightarrow H_2, \tag{2}$$

$$2\,OH^{\cdot} \longrightarrow H_2O_2. \tag{3}$$

The major portion of $H^{\cdot}$ atoms recombines inside a cavitation bubble, while the $OH^{\cdot}$ radicals recombine in solution after the bubble has collapsed.[5] The possible penetration of radicals from the cavitation bubble into the surrounding solution was confirmed by the spin trap method.[6] The isotope effect (α) for the generation of $H^{\cdot}$ and $D^{\cdot}$ atoms by the sonolysis of a 1 : 1 H_2O—D_2O mixture was found[7] to be 1.20—1.71. It was suggested that the isotope effect is caused by the homolytic cleavage of the O—H and O—D bonds, whereas dissociation of water molecules is due to adiabatic heating of the steam—gas mixture inside a cavitation bubble. However, some researchers[2] believe that dissociation of H_2O molecules can be induced by the electric discharge generated during the evolution of the cavitation bubble. Thus, the mechanism of water sonolysis requires further investigation. Study of the kinetic isotope effects in the H_2O—D_2, H_2O—HD, $H_2{}^{16}O$—$(^{18}O)_2$, $(^{14}N)_2$—$(^{15}N)_2$, and CH_4—D_2 isotope exchange processes, initiated by ultrasound, confirmed the formation of free radicals in the cavitation bubble.[5]

In this work, we study the isotope effect in the formation of hydrogen peroxide by the sonolysis of light and heavy water and discuss the probable mechanism of water sonolysis.

Experimental

Doubly distilled water (pH = 6.2) and freshly distilled heavy water (99.8% D_2O) were used in the experiments. Sonolysis was carried out in a thermostatically controlled cylindrical glass reactor with a working volume of the liquid of 20 mL using a UZDN-A ultrasonic disperser (the working frequency was 22 kHz and the maximum electrical power of the generator was 90 W). The disperser was equipped with a mushroom type titanium sonotrode with an effective radiating surface of 3.5 cm^2. The sonotrode was immersed into the liquid exposed to sonication in such a way that the distance from the radiating surface to the surface of the liquid was 4 cm. The sonotrode used was not eroded. The sonoreactor was covered by a plastic lid having holes for the sonotrode and for gas admission and escape and a capillary for sampling.

The acoustic power absorbed (P_{ac}) was determined by calorimetry using the procedure described previously.[3] The ultrasound intensity (I) was calculated by the equation $I = P_{ac}/S$, where S is the radiating area of the sonotrode (3.5 cm^2).

The gas for saturation (argon or oxygen) was bubbled through the liquid being sonicated for 30 min before and during the sonolysis. The gas flow rate was 100±20 mL min^{-1}.

The temperature inside the sonoreactor (20 °C) was maintained by circulation of cold water. It was found experimentally

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 4, pp. 645—649, April, 2000.

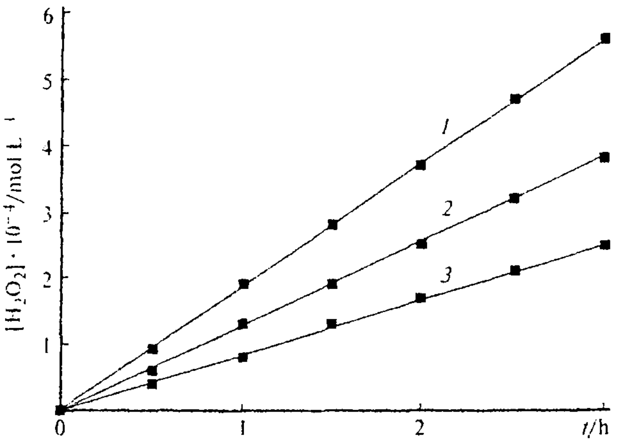

Fig. 1. Kinetic curves for the formation of hydrogen peroxide in the sonolysis of H_2O-D_2O mixtures in an Ar atmosphere: (*1*) H_2O, (*2*) H_2O-D_2O (1 : 1), (*3*) D_2O.

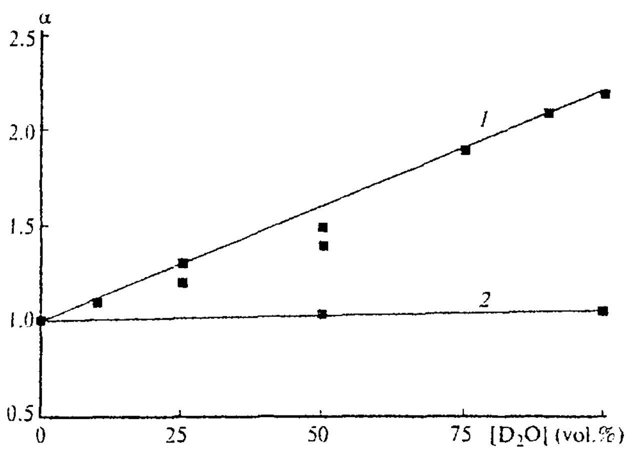

Fig. 2. Isotope effect (α) *vs* composition of the H_2O-D_2O mixture under Ar (*1*) and O_2 (*2*).

that a constant temperature was established 10 min after the beginning of sonolysis.

Samples for analysis were taken from the liquid being sonicated at definite intervals. The total concentration of hydrogen peroxide (H_2O_2, HDO_2, or D_2O_2) was determined by spectrophotometry using the molybdate-catalyzed reaction with potassium iodide.[8] The molar extinction coefficient (ε) of the resulting I_3^- ion at λ = 350 nm was found to be 22500 L mol^{-1} cm^{-1}.

The rate of formation of hydrogen peroxide ($W_{H_2O_2}$) was determined from the equation

$$W_{H_2O_2} = \Delta[H_2O_2]/\Delta t,$$

where $[H_2O_2] = \Sigma([H_2O_2] + [HDO_2] + [D_2O_2])$.

Results and Discussion

It follows from the kinetic curves of the formation of hydrogen peroxide (Fig. 1) that the process follows zero-order kinetics for at least 3 h of sonolysis. This result is in good agreement with the known data on the kinetics of sonolysis of light water.[3–5]

Study of the influence of the composition of the H_2O-D_2O mixture and the gas being bubbled on the rate of hydrogen peroxide formation (Table 1) showed that under argon the rate of hydrogen peroxide formation in light water is higher than in heavy water and that an increase in the concentration of D_2O diminishes *W*. The isotope effect (α), which is equal to the ratio of the reaction rates in H_2O and D_2O, is $\alpha = W_{H_2O}/W_{D_2O}$ = 2.2±0.3 when measured in argon (see Table 1). The α value observed in H_2O-D_2O mixtures increases almost linearly upon an increase in the D_2O concentration (Fig. 2).

Table 1. Rates of the sonochemical formation of hydrogen peroxide ($W_{H_2O_2}$) for various compositions of the H_2O-D_2O mixture

$[D_2O]$ (% v/v)	$W_{H_2O_2} \cdot 10^6$ /mol L^{-1} min^{-1}	$[D_2O]$ (% v/v)	$W_{H_2O_2} \cdot 10^6$ /mol L^{-1} min^{-1}
0	3.1±0.2	75	1.6±0.2
10	2.9±0.3	90	1.5±0.1
25	2.5±0.3	100	1.4±0.08
25	2.6±0.2	0*	1.3±0.1
50	2.3±0.2	50*	1.25±0.09
50	2.1±0.3	100*	1.23±0.08

Note. Experimental conditions: 22 kHz, I = 3.0 W cm^{-2}, P_{ac} = 0.52 W mL^{-1}, V = 20 mL, T = 20 °C, Ar. * In the presence of O_2.

Under otherwise identical conditions, the rate of formation of H_2O_2 from H_2O in an oxygen atmosphere is approximately 2.4 times lower than that under argon (see Table 1). This result is in good agreement with published data,[8] according to which the yield of H_2O_2 produced by the sonolysis of H_2O at an ultrasound frequency of 20 kHz and in argon is higher than that in oxygen. The formation of D_2O_2 in D_2O occurs at approximately equal rates in argon and oxygen atmospheres. No isotope effect was observed in an oxygen atmosphere (see Table 1, Fig. 2).

The isotope effect found cannot be explained by the difference between the physicochemical properties of H_2O and D_2O because the differences between the vapor pressure, viscosity, and heat capacity values do not exceed[9] 15–20%. In addition, the substantial influence of the gas used for saturation indicates that the isotope effect is most likely due to processes that occur in the gas phase of the cavitation bubble.

As noted above, hydrogen peroxide is formed in an argon atmosphere as a result of recombination of $OH^{\cdot}$ radicals, which is not accompanied by a substantial isotope effect. The interpretation of the $H^{\cdot}/D^{\cdot}$ isotope effect observed in water sonolysis in terms of the "classical" dissociative mechanism is based on the assumption that heating of the steam—gas phase of the cavitation bubble is an adiabatic process.[7] According to published data,[1–5] the temperature inside the bubble can reach 3000—5000 K. In the case of adiabatic heating, the process occurs under conditions of thermodynamic equilibrium, expressed by the equality $T_g = T_v = T_e$, where T_g, T_v, and T_e are translation, vibration, and electron temperatures of the gas, respectively. Then the kinetic isotope effect can be approximated by the equation[10]

$$\alpha = e^{E/RT}, \tag{4}$$

where $E = 1.24$ kcal mol^{-1} for homolytic dissociation of water molecules and T is the effective temperature inside a cavitation bubble. Using Eq. (4) and the α value determined experimentally, we found that the temperature inside a cavitation bubble is ~800 K. The calculated T value is much lower than that predicted by the adiabatic heating model or that found experimentally for cavitation in alkanes (~5000 K).[4] Moreover, the degree of dissociation of water molecules at 800 K is fairly low.[11] Thus, the observed isotope effect cannot be interpreted in the context of the adiabatic heating theory.

It would be of interest to compare the results obtained here with the data[7] on the isotope effect observed in the formation of $H^\cdot$ and $D^\cdot$ atoms upon water sonolysis. In view of reactions (1)—(3), the isotope effects for $H^\cdot/D^\cdot$ and H_2O_2/D_2O_2 (or $OH^\cdot/OD^\cdot$) are expected to be close. However, in experiments performed under conditions similar to those employed in this work (a 1 : 1 H_2O—D_2O mixture, operation frequency 50 kHz, Ar, $T = 25$ °C), the isotope effect was found to be 1.28—1.71. This is much lower than the α value characterizing the formation of hydrogen peroxide. In our opinion, α values reported in the literature[7] are underestimated due to the following reasons.

1. These data were obtained in experiments[9] with H_2O—D_2O mixtures (1 : 1) in which ~48% of the water molecules were HDO. The intramolecular isotope effect for HDO should be close to the intermolecular isotope effect (H_2O/D_2O) only for the case of the "classical" dissociative mechanism described by Eq. (4). If water sonolysis follows a different mechanism, intra- and intermolecular isotope effects may be dissimilar. The isotope effect observed in the formation of hydrogen peroxide depends substantially on the content of heavy water in the H_2O—D_2O mixture (see Fig. 2). The α value found in this study for an equimolar H_2O—D_2O mixture is equal to 1.4—1.5 (see Fig. 2), which is close to the published[7] $H^\cdot/D^\cdot$ value.

2. A substantial portion of the $H^\cdot$ ($D^\cdot$) atoms formed in reaction (1) recombines inside the cavitation bubble; only a small portion penetrates into the solution after the collapse and retains the ability to react with spin traps. The recombination of atoms might decrease the observed isotope effect, measured by the method of spin traps.

3. The observed $H^\cdot/D^\cdot$ isotope effect depends on the nature of the spin trap[7] (the α values for POBN (α-(4-pyridyl)-1-oxy)-*N-tert*-butylnitrone) and DMPO (5,5-dimethyl-1-pyrrolidine *N*-oxide) are 1.20 and 1.71, respectively). Side processes normally decrease the observed isotope effects.[10] Therefore, α = 1.71 can be considered to be closer to the real value than 1.20. According to Eq. (4), the value α = 1.71 matches a collapse temperature equal to 1200 K, which is also much lower than the temperatures predicted by the theory of adiabatic heating. Thus, analysis of the published data on $H^\cdot/D^\cdot$ isotope effects shows that, as in the case of the formation of hydrogen peroxide, this isotope effect cannot be interpreted within the framework of the "classical" adiabatic heating theory.

The magnitude of the isotope effect found might be due to fast energy exchange processes involving excited or ionized particles similar to the processes that occur in nonequilibrium plasma.[12] According to the modern views, two possible mechanisms of the formation of nonequilibrium plasma upon cavitation collapse are possible, namely, electric discharge[2] and shock wave.[13,14]

A nonequilibrium plasma generated by an electric discharge is characterized by a fairly high degree of ionization ($T_e \approx T_v > T_g$); therefore, electron impact and recharge processes play a crucial role in the dissociation of water molecules.[12] In this case, sonolysis of water can be represented by the following scheme:

$$\mathrm{Ar}\ (^1S_0) + e^- \longrightarrow \mathrm{Ar}^+ + 2\ e^- \qquad (E \geq 15.2\ \mathrm{eV}), \tag{5}$$

$$H_2O + e^- \longrightarrow H_2O^+ + 2\ e^- \qquad (E \geq 12.6\ \mathrm{eV}), \tag{6}$$

$$\mathrm{Ar}^+ + H_2O \longrightarrow \mathrm{Ar} + H_2O^+ \qquad (E \geq 12.6\ \mathrm{eV}), \tag{7}$$

$$H_2O^+ + H_2O \longrightarrow H_3O^+ + OH^\cdot, \tag{8}$$

$$H_2O^+ + e^- \longrightarrow H_2O^* (^3B_1) \longrightarrow H^\cdot + OH^\cdot, \tag{9}$$

$$H_2O + e^- \longrightarrow H^\cdot + OH^-. \tag{10}$$

Hereinafter, the steps of radical recombination are omitted. The concentration of argon atoms in a cavitation bubble is substantially higher than the concentration of water molecules; therefore, primary ionization (6) and heterolytic dissociation (10) of water molecules can be neglected. No data on the isotope effects in the dissociation of water molecules in an electric discharge are available; however, reactions giving rise to $OH^\cdot$ radicals in electric discharge ((8) and (9)) are similar to the processes giving $OH^\cdot$ radicals in water radiolysis ((12) and (13)) in an inert atmosphere[15,16]:

$$H_2O \overset{\wedge\wedge}{\longrightarrow} H_2O^+ + e^-, \tag{11}$$

$$H_2O^+ + H_2O \longrightarrow H_3O^+ + OH^\cdot, \tag{12}$$

$$H_2O^+ + e^- \longrightarrow H_2O^* (^3B_1) \longrightarrow H^\cdot + OH^\cdot, \tag{13}$$

where the character "^^→" implies "direct" action of ionizing radiation on water molecules. The isotope effect in the formation of hydrogen peroxide in the radiolysis of light and heavy water is close[15] to 1.2. The similarity of processes (8), (9) and (12), (13) suggests that the isotope effect observed in the case of electric discharge is also relatively small.

The close values for the isotope effects involved in electric discharge and radiolysis provide only indirect evidence for the fact that electric discharge is not the main cause of water sonolysis. There are more direct pieces of evidence pointing to a low degree of gas ionization in a cavitation bubble. If the set of reactions (5)—(10) were correct, water sonolysis would be expected to give not only H atoms and $OH^{\cdot}$ radicals but also solvated electrons e^-, which is the case for water radiolysis.[15,16] However, it was shown[17] that the yield of solvated electrons in water sonolysis is negligibly small. Moreover, it is known[3–5] that the rate of formation of H_2O_2 in the sonolysis of water in a Xe atmosphere is higher than that in an Ar atmosphere, although the ionization potential of Xe (12.13 eV) is lower than the ionization potential of water and the recharge step (7) cannot be effective in the presence of Xe.

In terms of the theory that assumes the development of a shock wave upon the collapse of a cavitation bubble, sonolysis of water in an argon atmosphere can be represented by the scheme

$$\mathrm{Ar} \text{)))}\!\!\rightarrow \mathrm{Ar}^{*}\ (\mathrm{Ar}\ (^{3}\mathrm{P}_{0,1,2})) \qquad (E = 11.55\ \mathrm{eV}), \tag{14}$$

$$\mathrm{H_2O} \text{)))}\!\!\rightarrow \mathrm{H_2O}^{*}\ (^{3}\mathrm{B}_1) \qquad (E = 9.5\ \mathrm{eV}), \tag{15}$$

$$\mathrm{Ar}^{*} + \mathrm{H_2O} \longrightarrow \mathrm{H_2O}^{*} + \mathrm{Ar}, \tag{16}$$

$$\mathrm{H_2O}^{*} \longrightarrow \mathrm{H}^{\cdot} + \mathrm{OH}^{\cdot}, \tag{17}$$

where the character ")))→" implies the cavitation excitation of atoms or molecules. According to the model in question, excitation is brought about by collisions of particles at the shock wave front. Since the concentration of Ar atoms in a cavitation bubble is higher than the concentration of water molecules, the contribution of reaction (15) to the overall process should be low. The probability of the $Ar^* \rightarrow H_2O$ transfer of energy is fairly high; it increases from 0.12 to 0.35 as the temperature rises from 200 to 3000 K.[18] In terms of the mechanism in question, the isotope effect can be accounted for by the different probabilities of energy transfer upon different types of collisions, $Ar^* \rightarrow H_2O$, $Ar^* \rightarrow D_2O$, and $Ar^* \rightarrow HDO$. The probability of the $Ar^* \rightarrow H_2O$ transfer of energy in the 200—3000 K temperature range is about twice as high[18] as the probability of the $Ar^* \rightarrow D_2O$ process. The ratio of the probabilities of energy transfer is in satisfactory agreement with the observed isotope effect. No data on the probability of the $Ar^* \rightarrow HDO$ transfer of energy are available; however, it should presumably be intermediate between those for H_2O and D_2O. Homolytic dissociation of excited H_2O^*, D_2O^*, and HDO^* does not involve any isotope effect.

Nonequilibrium plasma generated by a shock wave differs from that created by an electric discharge by higher translation temperature and lower degree of ionization ($T_g > T_e = T_r$).[19] The low degree of ionization is due to the fact that the energy absorbed by ionization is compensated by the transfer of energy from the gas heated in a shock wave front to the electrons. The energy exchange between heavy species and electrons proceeds slowly because their masses are appreciably different; this markedly retards the rate of development of ionization. Argon atoms can be excited if the temperature in the shock wave front is at least of the order of 10^4 K. Calculation of the parameters of Ar plasma shows[19] that, for a translation temperature of the gas in the shock wave front equal to 10000 K, a steady-state degree of ionization is attained over a period of 100 μs. This is much longer than the period of collapse of a cavitation bubble, equal to ~1 μs at an ultrasound frequency of 20 kHz. Thus, the cavitation collapse is too rapid for gas molecules to ionize; hence, nonequilibrium homolytic processes (14)—(17) make the predominant contribution to the sonolysis of water molecules.

The absence of isotope effects in an oxygen atmosphere is apparently due to the change in the mechanism of formation of hydrogen peroxide. Oxygen molecules can be excited and dissociate under the action of cavitation.[5] In this case, H_2O_2 would result not only from dissociation of H_2O molecules and subsequent recombination of the $OH^{\cdot}$ radicals but also due to other processes:

$$\mathrm{O_2} \text{)))}\!\!\rightarrow 2\ \mathrm{O}^{\cdot\cdot} \qquad (E = 5\ \mathrm{eV}), \tag{18}$$

$$\mathrm{O}^{\cdot\cdot} + \mathrm{H_2O} \longrightarrow 2\ \mathrm{OH}^{\cdot}, \tag{19}$$

$$\mathrm{O_2} + \mathrm{H}^{\cdot} \longrightarrow \mathrm{HO_2}^{\cdot}, \tag{20}$$

$$2\ \mathrm{HO_2}^{\cdot} \longrightarrow \mathrm{H_2O_2} + \mathrm{H_2O}, \tag{21}$$

$$\mathrm{OH}^{\cdot} + \mathrm{HO_2}^{\cdot} \longrightarrow \mathrm{H_2O} + \mathrm{O_2}. \tag{22}$$

It is evident that reactions (19)—(21), similarly to radical recombination, should not be accompanied by noticeable isotope effects. The decrease in the rate of formation of H_2O_2 in an atmosphere of O_2 relative to that in an atmosphere of Ar can be due to both side reaction (22) and dissipation of the shock wave energy as a result of excitation and dissociation of O_2 molecules.

The results of this study demonstrate that the mechanism of sonolysis of H_2O is governed by processes in the nonequilibrium plasma generated by a shock wave in the gas phase of a collapsing bubble.

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Received July 6, 1999;
in revised form November 30, 1999