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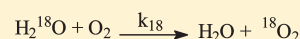
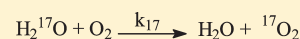
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Photo-oxidation of Water by Molecular Oxygen: Isotope Exchange and Isotope Effects

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ABSTRACT: Photolysis of $^{17,18}\text{O}$ -labeled water in the presence of molecular oxygen is accompanied by transfer of ^{17}O and ^{18}O isotopes from water to oxygen, demonstrating that photoinduced oxidation of water does occur. The reaction exhibits the following isotope effect: oxidation of H_2^{17}O is faster by 2.6% (in the Earth's magnetic field) and by 6.0% (in the field 0.5 T) than that of H_2^{18}O . The effect is supposed to arise in the two spin-selective, isotope-sorting reactions—recombination and disproportionation—in the pairs of encountering HO_2 radicals. The former is spin allowed from the singlet state; the latter occurs only in the triplet one. Nuclear spin sorting produced by these reactions proceeds in opposite directions with the dominating contribution of recombination, which provides observable $^{17}\text{O}/^{18}\text{O}$ isotope fractionation in favor of magnetic isotope ^{17}O . Neither isotope exchange nor the reaction itself occurs in the dark.



$$k_{17}/k_{18} = 1.03$$

Photo-oxidation of water by oxygen exhibits isotope effect: oxidation of H_2^{17}O is faster than that of H_2^{18}O

1. INTRODUCTION

Oxygen–water photoinduced reaction faces three problems: first, the ecology of natural water related to the synthesis of hydrogen peroxide under sunlight;¹ second, atmospheric photoinduced nucleation of water vapor into nanodroplets and fog formation; third, the intriguing problem of “magnetic” water, which was shown to exhibit sensitivity to the magnetic field in the presence of dissolved oxygen only.² Our attempts to directly detect oxygen–water reaction by measuring oxygen pressure over water or hydrogen peroxide in water failed because neither change of pressure nor H_2O_2 were detected. This means that either the reaction is immeasurably slow, or it is highly reversible.

In order to detect the reaction, we used water highly enriched with isotopes ^{17}O and ^{18}O , controlling the isotope composition of molecular oxygen before and after reaction. We observed transfer of both oxygen isotopes from the water into the molecular oxygen indeed as an indication of direct photoinduced reaction between water and oxygen.

2. EXPERIMENTAL SECTION

For the photolysis, two identical devices were used (Figure 1) in which quartz samples (thin-walled tubes of 10 mm diameter) were inserted through holes in the upper plates. In one of the devices, the pole pieces were made from magnetic iron (permanent magnetic field strength of 0.5 T); in the other one they were made from aluminum and imitated iron poles. Both were painted white to equalize intensities of scattered light. The sample tubes (the length of 12 cm) were filled two-thirds of the way with water (8 mL), and the volume over water was filled through the vacuum system with oxygen (700 mmHg). Only water was exposed to photolysis; the upper, oxygen-containing part of the tubes was closed by a screen opaque to light and was out of illumination. As a light source, a low-pressure mercury lamp (the power output $23 \mu\text{W}/\text{cm}^2$) was used with its long axis

oriented perpendicular to the axes of the sample tubes to provide equal intensities of their illumination. The unfiltered light was used with the following spectral distribution of intensity in the UV region: 15% in the range 230–300 nm, and 10% in the limits 300–330 nm. The total light stream was about $35 \times 10^3 \text{ lm}$ at a distance of 30 cm between the lamp and the equally distant sample tubes.

Photolysis was carried out by sessions of 5–9 h duration interrupted by switching on/off the lamp with dark intervals of 15–30 h. Transition periods of switching over when intensity was not constant were small in comparison with those of illumination (minutes versus hours). All system was installed in the ventilated box ($\sim 1 \text{ m}^3$) where temperature was kept by air flow in the range $22 \pm 2^\circ\text{C}$. The front wall of the tube was slightly (by 1 or 2°C) warmer than the back one; it favors mixing of gas and liquid by free flow of water. The total time of illumination was 920 h; the duration of the experiment was about 4700 h. In parallel, similar samples were kept in the dark 2 months (about 1400 h). As will be seen later, the possible minor difference in illumination of both samples has no importance because the main measured parameters (oxygen isotope compositions) were derived from the analysis of individual samples. Preliminarily we have tried to detect oxygen consumption by measuring oxygen pressure in the photo-oxidation (700 mmHg, duration of photolysis about 250 h) but observed no changes in pressure (in the limits $\pm 1 \text{ mmHg}$). Namely, from this disappointing result the idea to use isotopic water was stemmed.

Oxygen isotope composition of the water was determined by mass-spectrometric analysis of CO_2 generated in the reaction of isotope exchange between H_2O and K_2CO_3 ; the latter was decomposed by

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Figure 1. The view of the devices for the photolysis (see text). The connection with the vacuum system is not shown. Quartz tubes filled with water were placed between metal pole pieces on the Teflon stands.

Table 1. The $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ Values

isotope	before photolysis	after photolysis	
		$H = 0$	$H = 0.5 \text{ T}$
$\delta^{17}\text{O}, \text{‰}$	13.744 ± 0.043	37.601 ± 0.130	38.059 ± 0.130
$\delta^{18}\text{O}, \text{‰}$	26.958 ± 0.019	300.533 ± 0.019	299.961 ± 0.020

H_3PO_4 . This analysis, generally accepted for the multiply substituted isotopomers,³ takes into account isotope contents of ^{13}C in CO_2 generated from K_2CO_3 ; for this purpose, the intensities of signals with masses 44–49 in the mass spectra of CO_2 were detected.⁴ The measuring of isotope composition of molecular oxygen was carried out by a Delta^{plus} mass-spectrometer (Thermo, Bremen) in the dual inlet mode. Ion currents of signals with masses 32, 33, and 34 were registered simultaneously in the three collectors.⁵ All measurements were made with respect to generally accepted standard mean ocean water (SMOW) calibrated standard with accuracy given in Table 1. The errors of mass-spectrometric analysis are typical for the best modern mass-spectrometry.⁶ The technique of the preparation of oxygen samples for the mass-spectrometric analysis was routine and based on standard procedures, which include removal of traces of water and freezing out of O_2 by liquid nitrogen into a standard right angle glass sampler filled with zeolite NaX.⁵

3. RESULTS AND DISCUSSION

According to generally accepted practice of isotope measuring, we will express isotope composition of molecular oxygen in a δ -system:

$$\delta^{17}\text{O} = [(^{17}\text{R} - ^{17}\text{R}_{\text{st}})/^{17}\text{R}_{\text{st}}] \cdot 10^3\text{‰} \quad (1)$$

$$\delta^{18}\text{O} = [(^{18}\text{R} - ^{18}\text{R}_{\text{st}})/^{18}\text{R}_{\text{st}}] \cdot 10^3\text{‰} \quad (2)$$

Here $^{17}\text{R} = ([^{17}\text{O}]/[^{16}\text{O}])$ and $^{18}\text{R} = ([^{18}\text{O}]/[^{16}\text{O}])$ are the ratios of ^{17}O and ^{18}O content to that of ^{16}O , respectively, $^{17}\text{R}_{\text{st}}$ and $^{18}\text{R}_{\text{st}}$ are similar ratios for the standard, SMOW:⁵ $^{17}\text{R}_{\text{st}} = (373 \pm 15) \cdot 10^{-6}$, $^{18}\text{R}_{\text{st}} = (2005.2 \pm 0.43) \cdot 10^{-6}$.

3.1. Isotope Composition. The values of $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ for the starting oxygen (before photolysis) as well as for oxygen after

Table 2. Isotope Composition of Water $[\text{O}]_{\text{w}}$ and Oxygen before Photolysis $[\text{O}]_{\text{b}}$ and after Photolysis $[\text{O}]_{\text{a}}$

isotope	$[\text{O}]_{\text{b}}$	$[\text{O}]_{\text{a}}$		$[\text{O}]_{\text{w}}$
		$H = 0$	$H = 0.5 \text{ T}$	
^{16}O , at %	99.75685(0)	99.70141(0)	99.70149(1)	12.828 ± 0.002
^{17}O , at %	0.03772(1)	0.03858(6)	0.03861(0)	1.322 ± 0.002
^{18}O , at %	0.20542(5)	0.26000(4)	0.25987(2)	85.850 ± 0.010

photolysis in the Earth's magnetic field ($H = 0$) and in the field 5000 G ($H = 0.5 \text{ T}$) are presented in Table 1.

Both $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values exhibit remarkable properties. First, after photolysis, oxygen is strongly enriched with both isotopes, i.e., isotope exchange between water and oxygen does occur under photolysis. Second, no exchange and no reaction occur in the dark: δ -values were identical to those for the starting oxygen (13.742 ± 0.043 and $26.955 \pm 0.019 \text{‰}$ for ^{17}O and ^{18}O). Third, magnetic field simultaneously (in the same sample) slightly increases ^{17}O enrichment but decreases it for ^{18}O (see third and fourth columns in Table 1).

In order to transform these observations into quantitative results, it is necessary to calculate isotope composition of oxygen before and after photolysis. Equations 1 and 2 may be rewritten as follows:

$$^{17}\text{R} = (1 + 10^{-3}\delta^{17}\text{O})^{17}\text{R}_{\text{st}} \quad (3)$$

$$^{18}\text{R} = (1 + 10^{-3}\delta^{18}\text{O})^{18}\text{R}_{\text{st}} \quad (4)$$

Substituting $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$, as well as $^{17}\text{R}_{\text{st}}$ and $^{18}\text{R}_{\text{st}}$, one can calculate ^{17}R and ^{18}R . Then we calculate atomic shares ^{16}O , ^{17}O , and ^{18}O combining normalized equations:

$$^{16}\text{O} + ^{17}\text{O} + ^{18}\text{O} = 1 \quad (5)$$

$$^{16}\text{O} + ^{17}\text{R}^{16}\text{O} + ^{18}\text{R}^{16}\text{O} = 1 \quad (6)$$

The latter results to the following equation:

$$^{16}\text{O} = (1 + ^{17}\text{R} + ^{18}\text{R})^{-1} \quad (7)$$

Further, it is easy to calculate ^{17}O and ^{18}O as the products $^{17}\text{R}^{16}\text{O}$ and $^{18}\text{R}^{16}\text{O}$, respectively. These atomic shares (in atomic percents) are given in Table 2 for the starting oxygen (before photolysis, $[\text{O}]_{\text{b}}$) and oxygen after photolysis, $[\text{O}]_{\text{a}}$.

The balance of isotopic nuclei ^{17}O in oxygen is determined by additive relation:

$$m_{\text{a}}[^{17}\text{O}]_{\text{a}} = m_{\text{b}}[^{17}\text{O}]_{\text{b}} + ^{17}\alpha m_{\text{r}}[^{17}\text{O}]_{\text{w}} \quad (8)$$

Here m_{a} and m_{b} are the amounts of oxygen after and before photolysis, and m_{r} is that of the oxygen released from water during photolysis. The released oxygen inherits oxygen nuclei of water; however, isotope composition of oxygen is not identical to that of water because in the photolysis isotope fractionation does occur.

The coefficient $^{17}\alpha$ determines the probability that the oxygen molecule is released from H_2^{17}O . It is impossible to know the relation between oxygen consumed and oxygen released; however, taking into account that we have observed no change of oxygen pressure, one can suppose with high accuracy that oxygen consumed and oxygen released compensate each other, i.e., $m_{\text{a}} \approx m_{\text{b}}$.

Then from eq 8 follows

$$m_r/m_b = ([^{17}\text{O}]_a - [^{17}\text{O}]_b)/^{17}\alpha[^{17}\text{O}]_w \quad (9)$$

The balance of isotopic nuclei ^{18}O in oxygen is determined by relation similar to eq 8:

$$m_a[^{18}\text{O}]_a = m_b[^{18}\text{O}]_b + ^{18}\alpha m_r[^{18}\text{O}]_w \quad (10)$$

Now coefficient $^{18}\alpha$ determines the probability that the oxygen molecule is released from H_2^{18}O . Again, assuming that $m_a \approx m_b$, one can derive eq 11 similar to eq 9:

$$m_r/m_b = ([^{18}\text{O}]_a - [^{18}\text{O}]_b)/^{18}\alpha[^{18}\text{O}]_w \quad (11)$$

By combining eqs 9 and 11, one can derive the ratio $^{17}\alpha/^{18}\alpha$, which characterizes isotope effect in the photo-oxidation reaction:

$$\begin{aligned} & ^{17}\alpha/^{18}\alpha \\ &= \{([^{17}\text{O}]_a - [^{17}\text{O}]_b)/([^{18}\text{O}]_a - [^{18}\text{O}]_b)\} \{([^{18}\text{O}]_w/[^{17}\text{O}]_w)\} \end{aligned} \quad (12)$$

Substituting magnitudes of $[\text{O}]_a$, $[\text{O}]_b$, and $[\text{O}]_w$ into eq 12, one can determine the values of the isotope effect $^{17}\alpha/^{18}\alpha = 1.026 \pm 0.005$ (for $H = 0$) and 1.060 ± 0.005 (for $H = 0.5$ T). They demonstrate that the photo-oxidation of H_2^{17}O occurs by 3.3 and 3.7% faster than that of H_2^{18}O (in magnetic fields $H = 0$ and $H = 0.5$ T, respectively).

3.2. The Reaction Scheme. Isotope fractionation seems to be in accordance with classical, mass-dependent isotope effect (light H_2^{17}O water reacts faster than does H_2^{18}O); however, it is worth keeping in mind that, first, in the reactions of photoexcited states, classical isotope effect is usually very small and, second, as seen in Table 1, in the same sample subjected to photolysis in magnetic field, $\delta^{17}\text{O}$ slightly increases but $\delta^{18}\text{O}$ decreases in comparison with the sample in the Earth's magnetic field, i.e., magnetic field functions in opposite directions for ^{17}O and ^{18}O . Evidently, this effect can not be attributed to the possible minor difference in the light intensities for the two samples. Despite the fact that the magnetic field effect is not large, it gives certain evidence that in photo-oxidation reaction, a magnetic, mass-independent, isotope effect^{7–10} operates rather than a classical, mass-dependent one. Nevertheless, additional experiments are required to quantitatively characterize magnetic field effect on the water–oxygen reaction as a function of magnetic field, particularly keeping in mind that the magnetic isotope effect is not monotonous and has a maximum in the field comparable with the hyperfine coupling constant.¹⁰

Both isotope exchange and isotope effect reliably indicate that the photoinduced reaction between molecular oxygen and water does occur, and it is a radical, spin-selective reaction in which magnetic isotope effect functions.^{8–10} No doubt the reaction is accompanied by generation of H_2O_2 via the formation of hydroxyl radical as a primary intermediate. No photochemistry is thought to arise from direct excitation of water since its molecules do not have a strong absorption between 200–320 nm;¹¹ however, in the presence of dissolved oxygen, an enhancement of absorption of liquid water by up to 2 orders of magnitude in the region 200–300 nm was detected.¹¹ Moreover, there was found a correlation between oxygen-induced UV spectrum of liquid water and photonucleation spectrum of water vapor.^{12,13} On the basis of these facts, the existence of water–oxygen (WO) van der Waals complex was suggested, which

was assumed to transform into the charge transfer (CT) complex under photoexcitation.^{12–16} However, purely spectroscopic observations can not be considered as a conclusive indication of the WO complex. Another possible contribution to the O_2 -induced enhancement of the UV spectrum may appear to arise from collision-stimulated activation of forbidden optical transitions in dissolved oxygen for which symmetry or angular momentum restrictions are removed by collisions with water molecules.¹³

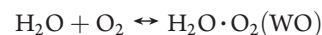
The most convincing evidence of the WO complexes follows from NMR of oxygen–water solutions. Paramagnetic shifts and NMR line broadening^{17–19} of the water hydrogen atoms unambiguously demonstrate that in the WO complex a transfer of unpaired electron spin density from the paramagnetic oxygen molecule to the water molecule takes place, i.e., common molecular orbitals combined from atomic orbitals of partners are formed. The magnitude of oxygen-induced paramagnetic shift, normalized to $[\text{O}_2] = 1$ M, is known to obey the equation

$$\delta = a\alpha K \quad (8)$$

Here

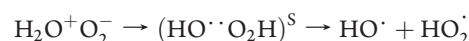
$$\alpha = -\hbar(\gamma_e/4\gamma_n kT) \quad (9)$$

a is the hyperfine coupling constant for hydrogen in the WO complex, and K is the equilibrium constant for reversible WO complex formation:



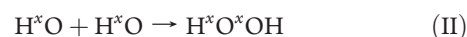
For the water hydrogen atoms in water–acetone solutions²⁰ δ is $-0.52 \text{ ppm} \cdot \text{M}^{-1}$. Combining eqs 8 and 9 one can determine only product $aK = 2.5 \times 10^{-3} \text{ G} \cdot \text{M}^{-1}$. Note, that NMR line of the water protons is shifted into the high field, that is transferred spin density is negative.^{17,18} One can conclude that in the WO complex positive π -electron spin density from oxygen molecule migrates into the lone pair of ligand, like in the similar complexes of nitroxyl radicals with water and hydroxyl-containing molecules. Then positive π -electron spin density via spin polarization of O–H bonds induces negative spin density on the ligand hydrogen atoms resulting in high field paramagnetic shifts of their NMR line. Besides of NMR paramagnetic shifts there are other evidence of oxygen–water complexes. Direct infrared identification of $\text{H}_2\text{O} \cdot \text{O}_2$ complex, isolated in rare gas matrix, was recently declared.²¹ At last, reliable kinetic evidence of CT complex $\text{H}_2\text{O}^+ \cdot \text{O}_2^-$ follows from the TOF mass spectrometry of the WO complexes.²²

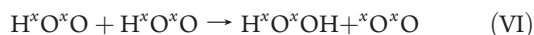
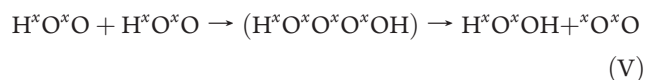
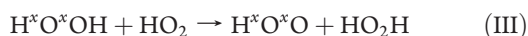
Taking into account that nothing but radical reactions may ensure isotope exchange between molecular oxygen and water, we will consider two oxygen-centered radicals, hydroxyl HO and peroxy radical HO_2 , which are responsible for exchange reactions. Both radicals are supposed to be born from intermediate radical pair generated from CT complex by intra- or intermolecular proton transfer:



(hereafter, the points indicating radicals will be omitted).

The HO and HO_2 radicals initiate chain reactions of propagation, termination, and chain transfer typical for any chain oxidative processes:





Here $x = 16, 17$, or 18 . The repetitive set of reactions I–VI ensures isotope exchange between molecular oxygen and water.

Now the question is what spin-selective reactions are responsible for the isotope fractionation and isotope effect. First of all, we should exclude among these reactions those in which OH radical participates. It has a very short electron spin relaxation time (about 10^{-11} – 10^{-12} s),^{23,24} so that in the pairs (HO OH), (HO O₂H) and primary pair (HO••O₂H)^S spin conversion occurs through the spin relaxation. Hyperfine ¹⁷O coupling contributes in it almost nothing and does not produce isotope fractionation. The only reactions responsible for the isotope fractionation are those of HO₂ radicals. Molecular oxygen arises in the reactions V and VI, which are spin selective and isotope sorting, they both proceed through the pairing of freely diffusing and encountering HO₂ radicals, in the encounter radical pairs (HO₂••O₂H). In these pairs, the population ratio of singlet and triplet states is determined by spin statistics and equals 1:3. Recombination reaction V is spin allowed from singlet state and generates tetraoxide H^xO^xO^xO^xOH, which is extremely unstable and decomposes, generating oxygen ^xO^xO from the central atoms. On the contrary, disproportionation reaction VI is spin allowed from triplet state, because it directly produces an oxygen molecule in the triplet ground state. Isotope fractionations produced by singlet–triplet conversion of singlet pairs and triplet–singlet conversion of triplet ones do not compensate each other because disproportionation reaction VI needs activation energy, and it is slow with respect to recombination reaction V. The latter reaction provides a dominating contribution into the isotope fractionation and enrichment of molecular oxygen with magnetic ¹⁷O isotope.

Spin conversion in the pair (HO₂••O₂H) is induced by hyperfine coupling on the terminal ¹⁷O atom of ¹⁷OOH radical (it is about 22G, like in the similar (CH₃)₃COO radical²⁵). This coupling accelerates singlet–triplet conversion of the pair and stimulates its dissociation. It results in slightly increased stationary concentration of peroxy radicals carrying an excess of ¹⁷O nuclei and bringing it into molecular oxygen again by reaction V, which functions as a cascade process of isotope fractionation.

It is important to note that spin conversion between singlet and triplet states is induced by hyperfine coupling in the ¹⁷O atoms of ¹⁷OOH and O¹⁷OH radicals, which is known to be almost identical for terminal and internal oxygen atoms (22G and 16.4G, respectively, for the related (CH₃)₃COO radical²⁵). It means that both O₂ and H₂O₂, generated in reactions V and VI should be enriched with ¹⁷O: the former accepts terminal oxygen atoms from the ¹⁷OOH radical, and the latter includes the internal atom of the O¹⁷OH radical. This prediction seems to agree with the observation that in H₂O₂ contained in rainwater the values δ¹⁷O slightly exceeds those predicted by the relation δ¹⁷O = 0.511 δ¹⁸O, which characterizes mass-dependent isotope effect.^{1,26}

4. CONCLUSION

Oxygen isotope exchange between water and molecular oxygen reliably demonstrates that photoinduced oxidation of water does occur. Despite the fact that the efficiency of isotope conversion is rather low (it does not exceed 10^{-3} for more than 900 h of photolysis), the quantum yield of the reaction itself may appear to be higher due to the partly reversible photochemical generation and decay of H₂O₂. The idea to use an isotope exchange reaction between water and molecular oxygen as a test reaction may appear to be valuable and may be exploited for various purposes. This ecologically significant reaction of global importance can be inhibited, accelerated, or catalyzed by many factors (metal ions, traces of organics, surface effects, etc.) and all these factors may be separately studied and controlled by detecting the isotope composition of oxygen with respect to that of water.

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