Chemical Physics Letters 693 (2018) 107–113

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Research paper

Experimental studies of the oxygen isotope anomalies ($\Delta^{17}O$) of H_2O_2 and their relation to radical recombination reactions

Tatiana A. Velivetskaya *, Alexander V. Ignatiev, Victoria V. Yakovenko, Sergey V. Vysotskiy

Far East Geological Institute, Far Eastern Branch of the Russian Academy of Sciences, Prospect 100-letya Vladivostoku 159, Vladivostok 690022, Russia

ARTICLE INFO

Article history:
Received 2 August 2017
In final form 7 January 2018
Available online 9 January 2018

Keywords:
Mass-independent fractionation
Oxygen isotope
H_2O_2
Water dissociation

ABSTRACT

The presence of oxygen isotopic anomaly in hydrogen peroxide (H_2O_2) has been established by measurements of three oxygen isotopes (^{16}O, ^{17}O, ^{18}O) in H_2O_2 from experiments on H_2O_2 formation using a water vapour discharge in presence of (O_2, CO_2, Ar) gases and using VUV photolysis of water vapour. The termolecular OH recombination reaction may be account for the source of MIF in H_2O_2 due to a selective isotopic enrichment through the radical pair mechanism with non-equivalent nuclei. It was established that the magnitude of the observed MIF signals in H_2O_2 depended on the presence of oxidising gases.

1. Introduction

Since the mass-independent fractionation of oxygen isotopes (O−MIF) has been first revealed in ozone (O_3) in laboratory experiments [1] and observed in a variety of atmospheric species [2], much theoretical [3–5] and experimental [3,6–8] effort has been applied toward understanding a mechanism for mass-independent fractionation of ^{17}O isotope. However, detailed processes and mechanisms that cause the O−MIF in the atmospheric oxygen-containing species are still not fully clarified. The study of mass-independent isotope fractionation processes has not only fundamental interest, but such studies contribute to a deeper insight into the chemistry of atmospheric species in terms of their sources and sinks, and controlling and maintaining of total atmospheric composition.

It is now believed [4] that photochemically formed ozone in the upper atmosphere is the primary source of O−MIF in a variety of atmospheric oxygen-contained gases; a large positive MIF signal of ozone is subsequently propagated *via* chemical reaction mechanisms to other oxygen atmospheric gases, such as CO_2, N_2O, H_2O_2. In particular, for hydrogen peroxide (H_2O_2) that produced in the gas-phase atmospheric reactions, the origin of the MIF measured in H_2O_2 in rainwater [9] may be related to the MIF from O_3 that is transferred to HO_2 *via* reaction of O_3 and OH, and then to H_2O_2 *via* recombination reaction of HO_2 [4]. The data obtained from laboratory experiments, on the other hand, show that there are a number of other reaction mechanisms which may produce O−MIF in H_2O_2. From experiments of Savarino and Theimens [10] on H_2O_2 producing in the H_2−O_2 reaction system, it was suggested that the origin of MIF is related to the reaction $H + O_2 + M \rightarrow HO_2 + M$, with M being a third body that stabilizes the association complex. Mass-independent fractionation of H_2O_2 has been also observed in experiments of Velivetskaya et al. [11] on H_2O_2 formation by a water vapour discharge under oxygen-free conditions.

Experiments of Velivetskaya et al. [11] reviled that the magnitude of MIF in H_2O_2 depended on concentrations of O_2 in the reaction system. This peculiarity in the MIF behavior caused reasonable interest to study **how** the MIF of H_2O_2 would be depended on the presence of some atmospheric gases. This motivated us to extend our experimental investigations to reaction systems for producing H_2O_2 by water vapour discharge in the presence of some oxidizing gases (O_2 and CO_2) and an inert gas (Ar) in a wide range of their concentrations.

In this paper we suggest the possible explanation for the origin of ^{17}O-excess in H_2O_2 in terms of concepts of free radical pair mechanism, applying to the formation of H_2O_2 by self reaction of two OH radicals. Based on experimental results on the bath gas and concentration dependence of MIF in H_2O_2, possible mechanisms are considered which can contribute to MIF signature in H_2O_2.

2. Experimental methods

In this work, two different methods were applied to generate H_2O_2. The first method was based on the water vapour discharge.

* Corresponding author.
E-mail addresses: velivetskaya@mail.ru (T.A. Velivetskaya), ignatev@fegi.ru (A.V. Ignatiev), yakovenko_v.v@mail.ru (V.V. Yakovenko), svys@mail.ru (S.V. Vysotskiy).

https://doi.org/10.1016/j.cplett.2018.01.012
0009-2614/

The discharge apparatus which was utilized in this study was essentially the same as that described in our previous paper [11] except for the spark gap between the tips of electrodes that was reduced to 30 mm. Briefly, the discharge was generated in a quartz chamber. During a run, the water vapour from the reservoir was passed with the He flow through the discharge chamber; condensable products of reactions were collected in the trap. An aliquot of the obtained sample was taken for oxygen isotope analysis. The other experimental details have been described earlier [11]. A number of experiments was performed with introducing O_2, CO_2, and Ar into the discharge chamber. The O_2 concentrations were changed between 0% and 25%; CO_2 and Ar concentrations were changed between 0% and 100%.

The second method was based on vacuum ultraviolet (VUV) irradiation of water vapour. We used a deuterium lamp (H2D2 lamp), type No. L11798-01, Hamamatsu Photonics, Japan. The VUV emission is dominated by 125 and 160 nm. The experiments were performed using a continuous purge system which mainly consisted of a photo-chamber with MgF_2 window, a reservoir for water, and a collected trap. After start of irradiation, the products of photolysis were collected in the trap. The duration of one experiment was approximately 1 h. An aliquot of the obtained sample was taken for oxygen isotope analysis.

A technique that was used to prepare a sample of H_2O_2 water solution for oxygen isotope analysis was the same as it described in our previous paper [11]. The method was based on oxidation of H_2O_2 by potassium permanganate ($KMnO_4$) in acid solution to liberate O_2 from H_2O_2 [9]. The typical reproducibility was obtained to be 0.16‰ and 0.24‰ for $\delta^{17}O$ and $\delta^{18}O$ [11]. Isotope ratio measurements were performed on an isotope ratio mass spectrometer MAT 253 running in a continuous flow mode. The other experimental details have been described earlier [11].

Oxygen isotope ratio are reported as conventional 'delta' notation that is defined as follows: $\delta = R_{sa}/R_{ref} - 1$, where R_{sa} and R_{ref} is the $^{18}O/^{16}O$ or $^{17}O/^{16}O$ ratio for the sample and internationally accepted reference material, respectively. Oxygen isotope ratios are given relative to the primary reference material Vienna Standard Mean Ocean Water (V-SMOW).Mass-independent fractionation of oxygen isotopes (oxygen isotope anomaly or ^{17}O-excess) are defined as $\Delta^{17}O$ values according to the expression: $\Delta^{17}O = \delta'^{17}O - \lambda \times \delta'^{18}O$, where the δ'-notation represents the following logarithmic expression: $\delta'^{17}O = 10^3 \ln(10^{-3}\delta^{17}O + 1)$ and $\delta'^{18}O = 10^3 \ln(10^{-3}\delta^{18}O + 1)$ which are commonly used to describe a linear relationship between oxygen isotope ratios with λ as coefficient, values of which vary in the range 0.509 to 0.530 for mass-dependent fractionation processes [12,13]. In this work, the value of λ = 0.528 for meteoric water [14,15] was used to determine $\Delta^{17}O$ values in H_2O_2 obtained in laboratory experiments.

3. Results

3.1. Isotopic ratios for H_2O_2 obtained in water vapour discharge experiments at no O_2-added conditions

A number of runs was made using laboratory standard of water with $\delta^{18}O$ value of −10.5‰. The average value of $\delta^{18}O$ and $\delta^{17}O$ for the obtained H_2O_2 was −8.08 ± 1.21‰ and −2.85 ± 0.69‰, respectively. A close similarity of the $\delta^{18}O$ values between the initial water and the product H_2O_2 is evident. The $\Delta^{17}O$ of H_2O_2 was estimated to be 1.43 ± 0.07‰. The yield of H_2O_2 was ~7.1 mmol/L. It was sensibly less in comparison with amounts of H_2O_2 (~32 mmol/L) produced in our previous work [11]. Some discrepancy is reasonable to be expected because the production of H_2O_2 is highly dependent on specific experimental conditions. Since different experimental setup were used in this and previous work, the amounts of H_2O_2 are not necessarily the same.

3.2. Effect of O_2 presence

The results of the experimental data for the isotope ratios and the yield of H_2O_2 are given in Table 1 and displayed in Fig. 1. The non-linear dependence was found for both isotope ratios and H_2O_2 production with respect to O_2 concentrations. It should be noted that the O_2 dependences presented here are investigated in more detail in comparison with our previous work, especially in the range of very low O_2 concentrations, and are extended to cover range of higher O_2 concentrations up to 25%. Although the lower amount of H_2O_2 was obtained in the present experiments, the agreement between previous and newly obtained $\Delta^{17}O$ and $\delta^{18}O$ values of H_2O_2 was surprisingly good at corresponding O_2 concentrations.

3.3. Effect of CO_2 presence

The results are given in Table 2 and displayed in Fig. 1. For CO_2 concentrations of 0.6–25%, the $\Delta^{17}O$ values tended to increase, but as CO_2 concentration approached to100%, they returned back to starting value again (Fig. 1b). The $\delta^{18}O$ values of H_2O_2 gradually increased as CO_2 was added (Fig. 1a). The H_2O_2 production was also altered by changing the CO_2 concentration in the gas mixture; the yield of H_2O_2 decreased as it shown in Fig. 1c.

Table 1
Amount and isotopic ratios of H_2O_2 for the H_2O–O_2 discharge experiments. In these experiments the O_2 concentrations were varied from 0.005% to 25%.

Run	O_2 concentrations in He,%	H_2O_2 in sample (mmol/l)	$\delta^{17}O_{SMOW}$ (‰)	$\delta^{18}O_{SMOW}$ (‰)	$\Delta^{17}O$ (‰)	N
1	0.005	7.4 ± 0.7	−2.34 ± 0.05	−7.10 ± 0.09	1.41 ± 0.07	4
2	0.013	7.7 ± 0.8	−1.45 ± 0.79	−5.49 ± 1.33	1.45 ± 0.19	6
3	0.02	8.6 ± 0.5	−0.55 ± 0.24	−4.16 ± 0.40	1.65 ± 0.04	4
4	0.04	7.6 ± 0.8	0.44 ± 0.24	−2.40 ± 0.43	1.71 ± 0.14	5
5	0.06	8.7 ± 0.3	2.20 ± 0.05	0.64 ± 0.17	1.86 ± 0.12	3
6	0.08	8.6 ± 0.8	3.19 ± 0.64	2.30 ± 0.90	1.97 ± 0.21	4
7	0.10	7.8 ± 1.1	4.10 ± 0.71	3.90 ± 1.27	2.04 ± 0.15	7
8	0.13	9.3 ± 1.8	4.89 ± 0.59	5.20 ± 1.35	2.14 ± 0.32	7
9	0.2	10.0 ± 1.8	8.34 ± 0.72	11.16 ± 1.20	2.45 ± 0.14	4
10	0.6	9.4 ± 2.0	9.31 ± 0.71	13.00 ± 1.26	2.45 ± 0.10	5
11	1.5	8.0 ± 0.3	10.64 ± 0.74	15.56 ± 1.41	2.43 ± 0.07	3
12	4.7	7.5 ± 1.4	9.67 ± 0.30	13.94 ± 0.65	2.32 ± 0.08	5
13	6.0	6.8 ± 1.6	9.42 ± 0.35	13.84 ± 0.79	2.12 ± 0.13	5
14	10	4.9 ± 1.0	8.85 ± 0.41	13.30 ± 0.54	1.84 ± 0.04	4
15	17	4.7 ± 0.9	7.00 ± 0.60	10.02 ± 1.10	1.72 ± 0.22	7
16	25	3.0 ± 0.7	5.19 ± 0.48	7.40 ± 0.96	1.28 ± 0.09	6

N is the number of repeated experiments at each O_2 concentration.