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# Hydrogen polyoxides $H_2O_3$ and $H_2O_4$ as components of peroxy radical condensate obtained from electro-dissociated water vapor

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ABSTRACT

The peroxy radical condensate synthesized from electro-dissociated water vapor has been investigated by the methods of Raman spectroscopy and chemical analysis of its decomposition products. It has been found that hydrogen peroxide $H_2O_2$ and trioxide $H_2O_3$ (besides water $H_2O$) are the main components. Also hydrogen tetroxide $H_2O_4$ is present in the PRC, but its amount is small. On heating, hydrogen tetroxide breaks down at the first step of the condensate decomposition in the solid phase; hydrogen trioxide chiefly disappears at higher temperatures during the decomposition in the liquid phase. These results make it possible to estimate the experimental value of hydrogen trioxide enthalpy of formation in the liquid solution, $\Delta_f H°_{220-250}(H_2O_3, aq.) = -32 \pm 4$ kcal/mol, from the thermochemical data, obtained in references Reznitskii et al. (1958) and Skorokhodov et al. (1959, 1961).

## 1. Introduction

Hydrogen polyoxides $H_2O_3$ (HOOOH) and $H_2O_4$ (HOOOOH) are of interest as the higher homologs of hydrogen peroxide [1], and also as the intermediates of some important processes of atmospheric and environmental chemistry (various reactions of ozone [2–8], “peroxone process” [9], radical–radical reactions $HO_2 + OH \rightarrow H_2O + O_2$ [10–13] and $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ [14–20] on singlet potential energy surfaces, and others); for review see [21–24]. Lately hydrogen polyoxides have received much attention in the literature [5–9,25–40], with most of the works being based on quantum chemical calculations; experimental papers deal mainly with hydrogen trioxide [5–9,25,26]. There is a comprehensive up-to-date review on this subject [23]. The only recent experimental works devoted to both hydrogen trioxide and tetroxide are our papers [33,34,39].

Hydrogen polyoxides are stable only at low temperature. The unique method of producing these substances in milligram to gram quantities is to prepare them as constituents of *peroxy radical condensates* (*PRCs*). PRCs are obtained on a cold surface (~80 K) by condensation of water vapor or other oxygen–hydrogen systems dissociated in a low-pressure electrical discharge. Upon heating above 150 K PRCs decompose with effervescence and yield gaseous oxygen and concentrated hydrogen peroxide solution [21,24,41]. The liberation of molecular oxygen is due to the decomposition of the active components according to the reactions $H_2O_3 \rightarrow H_2O + O_2$ and $H_2O_4 \rightarrow H_2O_2 + O_2$.[1] These chemical equations follow from the facts that molecular oxygen is the only gaseous product of PRC decomposition [21,24,41], and hydrogen peroxide does not break down during the process [41,42]. Detailed kinetic studies of hydrogen trioxide decomposition in organic solvents have shown that the primary products are water and singlet molecular oxygen; any other decomposition products (ozone, hydrogen peroxide) were not detected [23]. In aqueous medium, singlet oxygen undergoes very fast quenching to give ground-state $O_2$ [43].

Although thermochemical properties of hydrogen polyoxides are of fundamental importance, they have not yet been determined experimentally. In principle the values of hydrogen polyoxides enthalpies of formation can be derived from the experimental data [44–46] on the heat of decomposition of the PRC obtained from electro-dissociated water vapor. But this cannot be done unless the exact composition of this substance is known. The authors [44–46] considered hydrogen tetroxide $H_2O_4$ to be the active component of their condensates. Giguère et al. produced evidence for the presence of hydrogen trioxide $H_2O_3$ in the PRC from water

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*Abbreviations:* PRC, peroxy radical condensate.

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[1] In this paper, the chemical formula $O_2$ means molecular oxygen in its triplet ground state.

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vapor by studying both its IR and Raman spectra [47–49]. They reported fundamental vibrations of $H_2O_3$ oxygen frame, but one of the three frequencies disagrees with the modern data [33]. For hydrogen tetroxide $H_2O_4$ Giguère et al. was not able to observe the true set of its skeletal oscillations; see discussion in ref [33]. The vibrational spectrum of $H_2O_4$ oxygen frame (in the PRC from dissociated $H_2$–$O_2$ gaseous mixtures) has been characterized in detail only recently in the work [33].

The prime objective of the present study is to determine the chemical composition of the PRC synthesized from electro-dissociated water vapor (the content of hydrogen tetroxide $H_2O_4$, trioxide $H_2O_3$, and peroxide $H_2O_2$), and to elucidate which of the polyoxides is first to decompose on heating the condensate. Then on the basis of these findings an attempt is made to derive the enthalpies of formation of the hydrogen polyoxides from the experimental data of Refs. [44–46] on heat effects of the decomposition of the PRC from dissociated water vapor.

## 2. Experimental

Peroxy radical condensates were synthesized from the gas mixture of $H_2O$ and Ne dissociated at low pressure electrodeless microwave discharge in the same reactor as in the work [33]. By and large the experimental techniques were analogous to those used in Ref. [33]. The condensate was formed on the end cap of the reactor "finger" cooled with liquid nitrogen. The duration of synthesis was 90 min. Water vapor was admitted into the setup through a capillary connected with a vaporizer, containing degassed distilled liquid water. The vaporizer was not thermostated and was kept at room temperature (22–23 °C). Because of this water vapor flow rate varied from 1.5 L/h (STP) at the beginning of the synthesis to ~0.5 L/h at the end. The amount of $H_2O$ entered the reactor over the time of the experiment was $4.2 \cdot 10^{-2}$ mol. The neon gas flow rate was 0.56 L/h (STP). The setup was pumped by two for vacuum pumps (Vacfox VC-75 and GLD-201). The pressure during the synthesis was not controlled; it was determined by the pumping speed and input gases flow rate and took values below 0.5 mmHg. The discharge was sustained by a medical microwave generator Luch-11 (2450 MHz), the nominal output power was set to 12, 27, 42 or 60 W. The distance from the discharge cavity top to the bottom tip of the finger measured 3.5 cm.

For the determination of the PRC composition, the method of Raman spectroscopy was employed in combination with the chemical analysis of the decomposition products. Immediately after the synthesis, Raman spectra of the freshly prepared condensate were recorded by means of a Horiba Jobin Yvon LabRam HR 800 UV spectrometer (diffraction grating 1800 l/mm) with an external sensing unit ("superhead"). Green radiation (514.532 nm) of an ion argon laser was used for spectra excitation, the power at a sample being ~50 mW, exposition time 140 s.

Then liquid nitrogen was removed from the finger, the condensate heated up to room temperature and decomposed with the formation of gaseous $O_2$ and liquid $H_2O_2$ solution in water. The pressure during the decomposition was recorded with an electronic pressure gauge AIR-20/M2. The molar amount of evolved oxygen $N_{O_2}$ was estimated from the pressure vs. time curve, the volume being known. The $H_2O_2$ solution was quantitatively rinsed from the interior surface of the reactor, the molar amount of hydrogen peroxide $N_{H_2O_2}$ was determined by titration with $KMnO_4$. Water was not determined. We estimate relative errors of determination of $N_{O_2}$ and $N_{H_2O_2}$ not to exceed 4% and 7% respectively.

Also subject to Raman investigation was the partially decomposed condensate, which was prepared in the following way. At the moment during the heating when the condensate started to melt and decompose with some foaming, liquid nitrogen was poured into the finger. The melting and decomposition stopped, and on the finger remained the white foamed solid – the partially decomposed condensate.

The amounts of $H_2O_4$, $H_2O_3$ and $H_2O_2$ in the PRC can be calculated from the molar quantities of the decomposition products, $O_2$ and $H_2O_2$, and the relative intensities of $H_2O_4$ and $H_2O_3$ Raman peaks at 450 and 500 $cm^{-1}$. As the principal components of the PRCs are hydrogen tetroxide $H_2O_4$, trioxide $H_2O_3$, and peroxide $H_2O_2$ (as well as water $H_2O$), the following equations hold true,

$$\begin{aligned} &n(H_2O_2) + n(H_2O_4) = N_{H_2O_2}, \\ &n(H_2O_3) + n(H_2O_4) = N_{O_2}, \\ &n(H_2O_4)/n(H_2O_3) = R, \end{aligned} \tag{1}$$

where $n(H_2O_4)$, $n(H_2O_3)$ and $n(H_2O_2)$ are the quantities of the condensate components, $N_{H_2O_2}$ and $N_{O_2}$ are the quantities of the decomposition products, $R = a \cdot (I_{450} - I_{400})/(I_{500} - I_{400})$, $a = 0.92$ (see [33]), $(I_{450} - I_{400})$ and $(I_{500} - I_{400})$ are the intensities of $H_2O_4$ and $H_2O_3$ Raman peaks at 450 or 500 $cm^{-1}$ ($I_{450}$ and $I_{500}$ are the peak heights and $I_{400}$ is the background height taken at 400 $cm^{-1}$). Eqs. (1) can be solved to express the amounts of $H_2O_4$, $H_2O_3$ and $H_2O_2$ from the experimentally determined quantities,

$$\begin{aligned} &n(H_2O_4) = N_{O_2} \cdot R/(1 + R), \\ &n(H_2O_3) = N_{O_2}/(1 + R), \\ &n(H_2O_2) = N_{H_2O_2} - N_{O_2} \cdot R/(1 + R). \end{aligned} \tag{2}$$

The results of the composition determination (the values of $n(H_2O_2)$, $n(H_2O_3)$, and $n(H_2O_4)$) are not accurate. The main reason is that the peak of $H_2O_4$ at 450 $cm^{-1}$ is not clearly defined, which results in low precision of $R$. The second factor is the non-uniformity of the PRCs along their height. When using the expressions (2), the value of $R$ was assumed to be independent on the height. It was estimated as an average from several spectra of the same condensate taken from points different in altitude. In the Electronic Supplementary Material (ESI), examples of condensate Raman spectra at various altitudes (Fig. 2S), the values of $R$ and their averages (Table 1S) are given; the altitude scale is shown in Fig. 1S.

## 3. Results and discussion

The typical Raman spectrum of the PRC from dissociated water vapor is shown in Fig. 1 (spectrum A). In the range 400–900 $cm^{-1}$ the characteristic signals of hydrogen polyoxides skeletal oscillations can be observed [33]. The distinctive lines of $H_2O_3$ oxygen vibrations at 500 and 756 $cm^{-1}$, corresponding to OOO bend and asymmetric OO stretch modes, clearly exhibit themselves. The only characteristic signal of $H_2O_4$ detected in the spectrum is the peak at 450 $cm^{-1}$ (poorly defined and imperfectly resolved), belonging to its OOO bend 2 mode. The weaker lines of other $H_2O_4$ oxygen frame oscillations are hidden from view.

The most intense peak in the spectrum A (Fig. 1) with the maximum at 878 $cm^{-1}$ represents in the general case the superposition of three lines with maxima at 865, 878 and 881 $cm^{-1}$, belonging to symmetric OO stretch vibrations of $H_2O_4$, $H_2O_3$ and $H_2O_2$ respectively [33]. The lines 878 and 881 $cm^{-1}$ are always merged together; the line 865 $cm^{-1}$ can be visually distinguishable and observed as a shoulder if the concentration of $H_2O_4$ is substantial enough [33,39]. In the spectrum on Fig. 1 there is no apparent sign of this shoulder. These features of the spectrum lead to the conclusion that the amount of $H_2O_4$ in the condensate is low compared to that one of $H_2O_3$ and/or $H_2O_2$; the content of $H_2O_3$ is rather high.

In the range of wavenumbers greater than 1000 $cm^{-1}$, the lines of vibrations involving hydrogen atoms can be seen. The broad signal at ~1470 $cm^{-1}$ is caused by the HOO bending oscillations of