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Hydrogen polyoxides as components of peroxy radical condensates †

Alexander V. Levanov,[a] Oksana Ya. Isaikina,[a] Valerii V. Lunin [a, b]

[a] Department of Chemistry, Lomonosov Moscow State University
Leninskie Gory 1, stroenie 3, 119991 Moscow, Russian Federation
[b] A.V.Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences
Leninsky prosp. 29, 119991 Moscow, Russian Federation

The results of original studies dealing with methods of synthesis of low-temperature peroxy radical condensates, mainly composed of hydrogen tri- and tetroxides, hydrogen peroxide and water, are integrated and described systematically. The physicochemical properties of hydrogen tri- and tetroxides and the mechanisms of their formation as components of the peroxy radical condensates are considered.
The bibliography includes 169 references.

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I. Introduction

Hydrogen trioxide (H_2O_3) and tetroxide (H_2O_4) — the third and fourth members of the hydrogen peroxide homologous series after water and hydrogen peroxide [1] — are analogues of trisulfane, HSSSH (H_2S_3), and tetrasulfane, HSSSSH (H_2S_4), respectively. They have a chain structure, H—O—O—O—H and H—O—O—O—O—H, and, according to the IUPAC nomenclature, they are called trioxidane and tetraoxidane. The name 'higher hydrogen peroxides' is also used. Hydrogen polyoxides are of interest as intermediates of several important oxidation reactions that occur in the environment, in living organisms and in various industrial processes. First of all, these are reactions occurring on a singlet potential energy surface [2 – 12]

$$HO_2^{\bullet} + HO^{\bullet} \longrightarrow H_2O + O_2 \quad (1)$$

$$HO_2^{\bullet} + HO_2^{\bullet} \longrightarrow H_2O_2 + O_2 \quad (2)$$

and ozone-involving reactions,[13 – 20] in particular, the peroxone reaction.[17] Furthermore, hydrogen trioxide is formed upon water radiolysis [18 – 20] and, according to a publication,[21] it can be produced by antibodies during the immune response. The contemporary scientific periodicals widely cover the quantum chemical theoretical studies of hydrogen polyoxides;[13, 14, 16, 22 – 32] laboratory experiments have mainly addressed hydrogen trioxide.[13 – 17, 33 – 36] Experimental studies of H_2O_3 and H_2O_4 as components of peroxy radical condensates (PRC) are considered in several publications.[32, 37 – 39] Detailed reviews devoted to hydrogen trioxide,[40, 41] organic trioxides [42] and organic tetroxides [43] are available. In the mentioned reviews [42, 43] and in a monograph,[44] hydrogen tri- and tetroxides are considered in brief. The studies of PRCs performed before 1965 are summarized in a review [45] and in a monograph.[46]

A.V.Levanov. Candidate of Chemical Sciences, Associate Professor of the Division of Physical Chemistry at the Department of Chemistry, MSU.
Telephone: +7(495)939 – 3685, e-mail: levanov@kge.msu.ru
Current research interests: physical chemistry, chemical kinetics, spectroscopic techniques.
O.Ya.Isaikina. Candidate of Chemical Sciences, Senior Researcher of the Laboratory of Catalysis and Gas Electrochemistry at the Department of Chemistry, MSU.
E-mail: hadi1@yandex.ru
Current research interests: physical chemistry, peroxide compounds.
V.V.Lunin. Academician, Professor, Doctor of Chemical Sciences, Dean of the Department of Chemistry, MSU, Head of the Laboratory of Organic Catalysis at the TIPS RAS.
Telephone: +7(495)939 – 3571, e-mail: vvlunin@kge.msu.ru
Current research interests: physical chemistry, chemical kinetics, catalysis, peroxide compounds, carbon and carbon allotropes, metal hydrides.

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Currently, H_2O_3 has been characterized in a considerable detail: its vibrational spectra have been studied,[33, 39, 47] the molecular structure in the gas phase has been determined,[34] and decomposition kinetics have been measured in various solvents.[13, 14, 18–20, 36] As regards H_2O_4, some time ago there was reasonable doubt about the possibility of its existence in PRC, although initially particularly this species had been believed to be the major PRC component. Convincing evidence for the existence of H_2O_4 was obtained quite recently.[39]

The polyoxides H_2O_3 and H_2O_4 are quite unstable and can be stabilized only at low temperature. The only practical method for the synthesis of these compounds in milligram amounts (up to several tenths of a gram) is to prepare PRC. Recently, a method for the preparation of concentrated solutions of H_2O_3 in anhydrous diethyl ether at low temperature has been developed.[35] Pure H_2O_3 samples can be obtained by evaporating the diethyl ether from these solutions at reduced pressure. Peroxy radical condensates are yellowish glassy substances formed upon low-temperature ($\sim$77 K) condensation of H_2O and H_2O_2 vapours or $H_2 + O_2$ mixtures dissociated in electric discharge, or by the reaction of hydrogen atoms with liquid ozone or gaseous oxygen on a cold surface. The active PRC components are H_2O_3 and H_2O_4. Also, PRC contain 'common' H_2O_2, H_2O and up to 0.5 mass % of $HO_2^{\bullet}$ radicals. The physicochemical properties of PRC‡ are determined by their components, first of all, the polyoxides H_2O_3 and H_2O_4.

The present review addresses the formation mechanisms, the vibrational spectra, the kinetics and heats of decomposition of hydrogen tri- and tetroxides as PRC components and also the methods of synthesis and physicochemical properties of the condensates themselves. In order to give the full picture of the research in this area, we considered not only recent publications, but also earlier papers; the results obtained since the 1970s and up to now are integrated and described systematically.

II. Synthesis of peroxy radical condensates and composition of PRC decomposition products

Several methods are known for PRC synthesis: condensation of the products of reaction between atomic hydrogen and gaseous oxygen and ozone;[48] condensation of $H_2 + O_2$ mixtures or H_2O/H_2O_2 vapours dissociated in an electric discharge; and reaction of hydrogen atoms with liquid ozone.[49, 50]

The efficiency of PRC synthesis is affected by the reactor design and size, the pressure and the temperature of the synthesis, the composition and the flow rate of the initial gas mixture and the discharge power. The reactors used for this synthesis (Fig. 1) are basically composed of three parts: the discharge zone, the synthesis zone (low-temperature trap) and the connecting channel between the discharge and synthesis zones. Under the discharge, the initial gases or vapours dissociate into atoms and radicals. Along the connecting channel, they are delivered into the trap. The peroxy radical condensates are formed upon chemical reactions of atoms and radicals on the walls of the low-temperature trap.

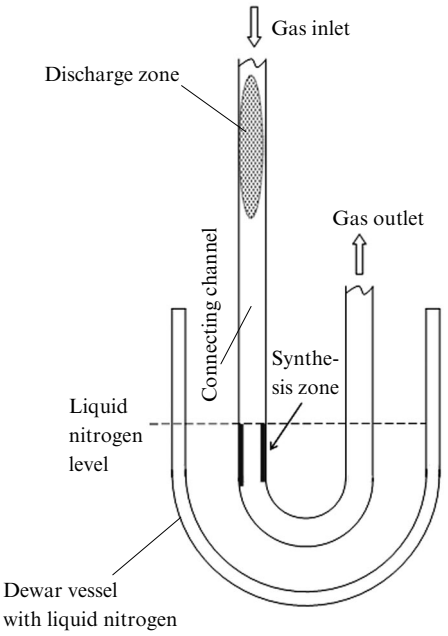


Figure 1. Basic diagram of the reactor for PRC synthesis (a possible design).

It was found in special experiments[51] that increasing the temperature of the trap above the liquid nitrogen temperature, all other conditions being invariable, leads to decreasing yields of the active PRC components. If the temperature of PRC synthesis is lower than 150 K, oxygen is released upon heating of the condensate, which is indicative of the presence of H_2O_3 and H_2O_4 as condensate components. When the synthesis temperature is 150–190 K, no oxygen is released and the condensate is found to contain only H_2O_2 and H_2O. In the case of synthesis temperature >190 K, the condensed product consists only of H_2O.[51]

For the highest yields to be obtained, the atoms and radicals formed in the discharge should reach the liquid nitrogen-cooled surface as fast as possible. When a surface with an intermediate temperature, in particular, the connecting channel, is located on their way, the yield considerably decreases because of the decay of some active species.[52] Therefore, the optimal design of the reactor does not include a connecting channel, with the discharge zone directly adjoining the freezing zone or coinciding with it. These requirements are met in the reactor representing a U-shaped gas discharge tube (characteristic diameter of $\sim$15 mm) immersed into liquid nitrogen (77 K). A reactor of this type was used for the first time by Kobozev *et al.*[53] Peroxy radical condensates are synthesized at a reduced pressure (0.5–1 mm Hg), which is usually created by a backing vacuum pump. The efficiency of the synthesis increases if the set pressure is as low as possible and cooled electrodes are used.

The peroxy radical condensate freezes out on the walls of the low-temperature trap (discharge tube) as a transparent, slightly yellow-coloured glassy material. On heating to room temperature, it decomposes to give a considerable amount of oxygen gas and a liquid aqueous solution of

‡ Note that a considerable part of studies of the PRC was performed at the Laboratory of Catalysis and Gas Electrochemistry of the Department of Chemistry, Moscow State University.

H_2O_2 (30 mass % – 60 mass %). The evolution of oxygen is caused by decomposition of the active components according to the reactions

$$H_2O_3 \longrightarrow H_2O + O_2 \quad (3)$$

$$H_2O_4 \longrightarrow H_2O_2 + O_2 \quad (4)$$

The PRC decomposition products [O_2(g) (see §), H_2O_2 and H_2O] are quantified in the following way.[54] The amount of oxygen $n(O_2)$, where n is the number of moles, is calculated from the pressure of the evolved gas collected in a definite volume. The amount of hydrogen peroxide $n(H_2O_2)$ in the liquid solution is found by potassium permanganate titration in sulfuric acid solutions by a standard procedure.[55] The amount of water $n(H_2O)$ is found from the total mass of the liquid solution and the amount of H_2O_2 it contains. Since the condensate is composed of four major components (H_2O_4, H_2O_3, H_2O_2 and H_2O) and two of them (H_2O_4, H_2O_3) decompose to give off oxygen, the condensate composition cannot be unambiguously determined from the results of chemical analysis of decomposition products.

An important role for determination of PRC composition is played by the ratio of the amounts of oxygen and hydrogen peroxide in decomposition products — $N_{O_2}/N_{H_2O_2}$. It is related to the amounts of components in the condensate that has not decomposed in the following way:

$$\frac{N_{O_2}}{N_{H_2O_2}} = \frac{n(H_2O_3) + n(H_2O_4)}{n(H_2O_2) + n(H_2O_4)} \quad (5)$$

These relations neglect the gas evolution as a result of recombination of $HO_2^{\bullet}$ free radicals and the presence of ozone and occluded molecular oxygen in the condensate. The contribution of these factors to the overall gas evolution is insignificant and the introduced error is, most often, lower than the error of experimental determination of $N_{O_2}/N_{H_2O_2}$.

The benefits of the $N_{O_2}/N_{H_2O_2}$ ratio are that it can be determined from commonly available chemical analysis data alone (without the necessity to quantify water) and that it generally reflects the 'quality' of the condensate: the higher the active component content in the PRC (hydrogen polyoxides as compared with H_2O_2), the greater this ratio. Furthermore, the $N_{O_2}/N_{H_2O_2}$ ratio is dimensionless and is barely affected by the time of synthesis. Previously (see, for example, Refs 52, 56 and 57), particularly the $N_{O_2}/N_{H_2O_2}$ ratio served as the key criterion of the efficiency of PRC synthesis, because H_2O_4 was believed to be the only active component. In this case, this ratio should have been in the range of 0 – 1; the ratio equal to unity would have indicated the presence of only H_2O_4 and water in the condensate. For the condensates formed in the reaction of hydrogen atoms with liquid ozone, the condition $N_{O_2}/N_{H_2O_2} = 1$ is always fulfilled. However, as shown by experiments,[32] these condensates contain comparable amounts of H_2O_2, H_2O_3 and H_2O_4. For most of the condensates, H_2O_3 is the predominant active component;[32, 37, 39] therefore, the $N_{O_2}/N_{H_2O_2}$ ratio can be both lower and higher than unity. Note that

§ The following designations are used: g, liq and s are gaseous, liquid and solid states, respectively; aq stands for aqueous solutions.

Table 1. $N_{O_2}/N_{H_2O_2}$ values for different methods for PRC synthesis.

Method of synthesis	$N_{O_2}/N_{H_2O_2}$	Ref.
Reaction $H^{\bullet} + O_2$ (g)	0.05 – 0.35	60 – 66
From electrically dissociated H_2O vapour	0.11 – 0.21	37, 67 – 76
From electrically dissociated H_2O_2 vapour	0.16 – 0.3	68, 76 – 79
Reaction $H^{\bullet} + O_3$ (g)	0.08 – 0.25	61, 66
Reaction $H^{\bullet} + O_3$ (liq)	1	49, 50, 77, 80
From electrically dissociated $H_2 + O_2$ gas mixtures of various composition	0.7 – 5	38, 53, 58

Berezin *et al.*[58] and Gromov *et al.*[59] managed to synthesize the condensates with very high $N_{O_2}/N_{H_2O_2}$ ratios.

The efficiency of PRC syntheses from different starting compounds can be evaluated considering the data of Table 1. For PRC synthesis, it is very convenient to use $H_2 + O_2$ gas mixtures. Variation of the composition of these mixtures gives rise to condensates with different contents of active components.

III. Vibrational spectroscopy of peroxy radical condensates

Vibrational spectroscopy is the most efficient method for determining the active PRC components and for studying their structures. Yagodovskaya and Nekrasov[81, 82] were the first to detect new bands (not attributable to known compounds such as H_2O, H_2O_2, O_3 or $HO_2^{\bullet}$) in the IR spectra of PRC. Quite a few new bands were found and assigned to hydrogen polyoxides, first, to H_2O_4, and then also to H_2O_3. The absorption bands in the 570 – 840 cm^{-1} range are likely to be caused particularly by vibrations of the oxygen skeleton of the polyoxides H_2O_3 and H_2O_4.

Convincing evidence for the presence of H_2O_3 in the condensate was reported in 1970 – 1974 by Canadian physical chemist Giguere and co-workers.[47, 83 – 85] Using IR and Raman spectroscopy, they observed the whole set of vibrational frequencies of the oxygen skeleton of hydrogen trioxide; the assignment of these bands was virtually the same as the modern assignment.

A full spectroscopic characterization of hydrogen trioxide was reported in 2002 by Engdahl and Nelander,[33] who investigated H_2O_3 isolated in a low-temperature argon matrix by IR spectroscopy. The lines for all nine fundamental vibrations of H_2O_3 were observed; the experimental vibrational frequencies were in very good agreement with the results of quantum chemical calculations.[23, 33, 39] In 2005, the geometric structure of the H_2O_3 molecule in the gas phase was determined with high accuracy by Fourier transform microwave spectroscopy.[34]

As regards H_2O_4, Giguere and co-workers were unable to identify the correct set of vibrational frequencies for the oxygen skeleton of this molecule. The frequencies that they assigned to hydrogen tetroxide generally do not agree with the results of modern quantum chemical calculations.[23, 28, 39] The later attempts to obtain H_2O_4 in a low-temperature matrix and to characterize it by IR spectroscopy have not met with success. Attempts were made to

prepare the higher peroxide H_2O_4 by photolysis of formaldehyde or glyoxal in an O_2 matrix at 15 K.[86,87] The photooxidation of these compounds gives two $HO_2^{\bullet}$ radicals and two CO molecules as the primary products. In the subsequent reactions, according to IR spectroscopy data, the $HO_2^{\bullet}$ radicals form a cyclic dimer $(HO_2^{\bullet})_2$ complexed with a CO molecule, but not a chain HOOOOH molecule. These conclusions were later confirmed in a theoretical study.[88] These results raised doubts about the possibility of existence of H_2O_4 in low-temperature condensates (matrices).

The modern and most detailed investigations of PRC by Raman spectroscopy were reported by Levanov *et al.*[39] The synthesis was carried out by condensation at 77 K of oxygen and hydrogen gases pre-atomized in a microwave discharge. The procedure was suitable for preparing samples containing considerable amounts of both polyoxides (H_2O_4 and H_2O_3). Therefore, it was possible to record intense Raman spectra of the condensates and to reliably characterize the polyoxides, including H_2O_4, on the basis of vibrational spectra of their oxygen skeletons. The experimental spectra of the polyoxides[39] are in good agreement with the results of high-level quantum chemical calculations.[23,28]

A typical Raman spectrum of PRC is shown in Fig. 2. In the 440 –890 cm^{-1} range, the spectrum contains clear-cut lines (they are designated by continuous arrows) that correspond to neither water nor hydrogen peroxide. These lines are due to the normal vibrations of the oxygen skeletons of the hydrogen polyoxides, which is supported by isotope substitution (deuterium for hydrogen). The other lines in the spectrum correspond to vibrations of OH groups (in the H_2O, H_2O_2, H_2O_3 and H_2O_4 molecules) and HOO groups (in H_2O_2, H_2O_3 and H_2O_4 molecules) and have analogues in the well-known hydrogen peroxide spectrum.[89] The intense broad band with a maximum at 3180 cm^{-1} corresponds to the stretching modes of hydrogen-bonded hydroxyl groups. The HOO bending modes give rise to the broad peak with a maximum at 1448–1468 cm^{-1}. The peak at 2840 cm^{-1} corresponds to a combined absorption band for the HOO bending mode. In the condensate of hydrogen peroxide or its mixtures with water, these lines occur at somewhat lower frequencies. When hydrogen is replaced by deuterium, the lines corresponding to OH and HOO vibrations shift to lower frequencies.

The broad unresolved signal (shoulder) at 40–380 cm^{-1} falls in the region that shows rather intense lattice modes in the spectrum of crystalline H_2O_2. Weak broad signals of the quartz glass, the reactor material, can be superimposed on the spectrum of the condensate in the 40–380 cm^{-1} range.

The strict assignment of the Raman lines of the condensates was based on a quantum chemical simulation of the vibrational spectra of the H_2O_4, H_2O_3 and H_2O_2 molecules.[39] The calculations were carried out by density functional theory (B3LYP) with the 6-31+G(d,p) basis set using the Gaussian 03 program package. The calculated vibrational frequencies were scaled by being multiplied by a factor equal to the ratio of experimental (881 cm^{-1}) and calculated (921 cm^{-1}) O–O stretching frequencies of the H_2O_2 molecule. In view of the strong intermolecular interactions (hydrogen bonds) in the PRC, comparison of the calculated and experimental frequencies makes sense only for vibrations of the polyoxide oxygen skeleton that do not affect the hydrogen atoms.

The vibrational spectra of molecules are related to their geometric structure. Quantum chemical calculations of the geometric structures of hydrogen polyoxide molecules have been reported in numerous publications;[23,24,27,28,90–92] earlier theoretical results have been summarized in reviews[42,43] and a monograph.[44] Apart from the paper of Levanov *et al.*,[39] calculations of vibrational spectra of H_2O_4 and H_2O_3 at a modern level have also been reported in other works.[23,28] The use of density functional theory[23,39] gives a satisfactory agreement with experimental data. However, the resulting vibrational frequencies are always overestimated. That is why Levanov *et al.*[39] used the scaling procedure while comparing the calculated and experimental frequencies. The correlated coupled-cluster methods,

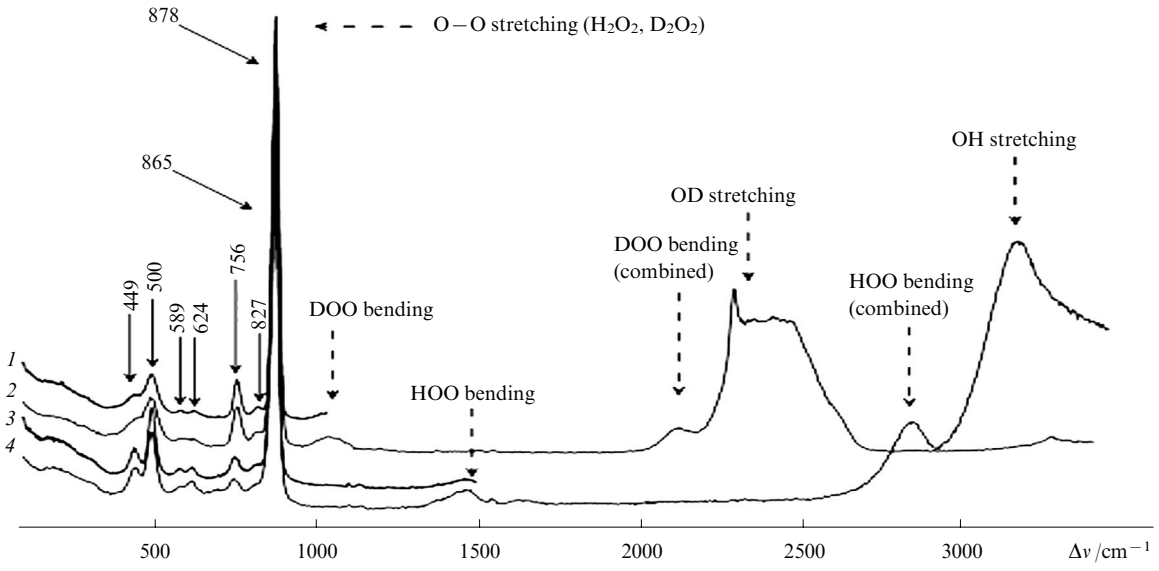


Figure 2. Raman spectra of PRCs synthesized from oxygen–deuterium (70 vol.% O_2 + 30 vol.% D_2O) (*1*, *2*) and oxygen–hydrogen (86 vol.% O_2 + 14 vol.% H_2) (*3*, *4*) systems.[39]

CCSD(T)/cc-pVTZ (Ref. 23) and CCSD(T)-F12/cc-pVTZ-F12 (Ref. 28), are much more perfect, as they are free from the above-mentioned drawback. The most accurate data on the vibrational spectra of hydrogen polyoxides were obtained by Hollman and Schaefer[28] by the CCSD(T)-F12/cc-pVTZ-F12 method. For most skeletal vibrations, the theoretical[28] and experimental[39] results were in good agreement.

The experimental vibrational frequencies of H_2O_4 and H_2O_3 as PRC components are also presented in the publications of Giguere and co-workers.[47,83–85] The O–O asymmetric stretching and OOO bending frequencies for H_2O_3 reported in these papers almost coincide with those found by Levanov *et al.*[39] However, the unresolved peak (shoulder) at $\sim$855 cm^{-1}, which was assigned by Giguere and co-workers to the O–O symmetric stretching mode of the H_2O_3 molecule, actually refers to a similar vibration of the H_2O_4 molecule, the exact frequency of the peak being 865 cm^{-1}. The line for the O–O symmetric stretching mode of hydrogen trioxide occurs at 878 cm^{-1}, which virtually coincides with the corresponding H_2O_2 line at 881 cm^{-1}. In the study of Levanov and co-workers,[39] the lines at 865 and 878 cm^{-1} were identified by numerical deconvolution of the contour of the peak at $\sim$880 cm^{-1}. Giguere and co-workers could not use this approach, because there were no appropriate computing resources at that time.

For H_2O_4, Giguere experimentally observed only two signals at 820–830 and 450 cm^{-1} (see Ref. 47 and references cited therein). The main cause is that the condensates contained only a minor amount of H_2O_4 (not more than 0.6 mol.%).[93] Other vibrational frequencies were based on the poorly defined experimental signals and on analogy between the vibrational spectra in homologous series of the polyoxides H_2O_n and polysulfanes H_2S_n. As a result, three (out of six) frequencies that were assigned to the H_2O_4 skeletal vibrations in the Giguere's work differed very sharply from both experimental values[39] and results of recent computational studies.[23,28,39] The condensates containing up to 20 mol.% H_2O_4 were obtained in experiments;[39] this allowed researchers to comprehensively characterize for the first time the vibrational spectrum of the oxygen skeleton of this compound.

The experimental Raman spectrum of PRC and the simulated spectra of the H_2O_2, H_2O_3 and H_2O_4 molecules are shown in Fig. 3.

Most of lines that correspond to the polyoxide oxygen skeleton do not overlap with one another. An exception is the most intense peak at $\sim$880 cm^{-1}, which is a superposition of three signals. This is especially evident in the experimental spectra of the mixtures enriched with oxygen, in which a shoulder at 865 cm^{-1} is clearly seen. The deconvolution of the peak at $\sim$880 cm^{-1} showed that it consists of three signals with maxima at 865, 878 and 881 cm^{-1}. The line at 881 cm^{-1} is caused by the O–O symmetric stretching vibration of the H_2O_2 molecule. The lines at 878 and 865 cm^{-1} correspond to analogous vibrations of H_2O_3 and H_2O_4.

The line for O_4 torsional vibrations is not manifested in the experimental spectra. This is quite predictable because, according to calculations, this line has low intensity in the Raman spectrum and, furthermore, it falls into the region of the broad unresolved shoulder at 50–400 cm^{-1}. This shoulder is present in all spectra and covers the weak line for the O_4 torsional vibrations. The published data on the vibrational frequencies of the oxygen skeleton of hydrogen tri- and tetroxide molecules are summarized in Table 2.

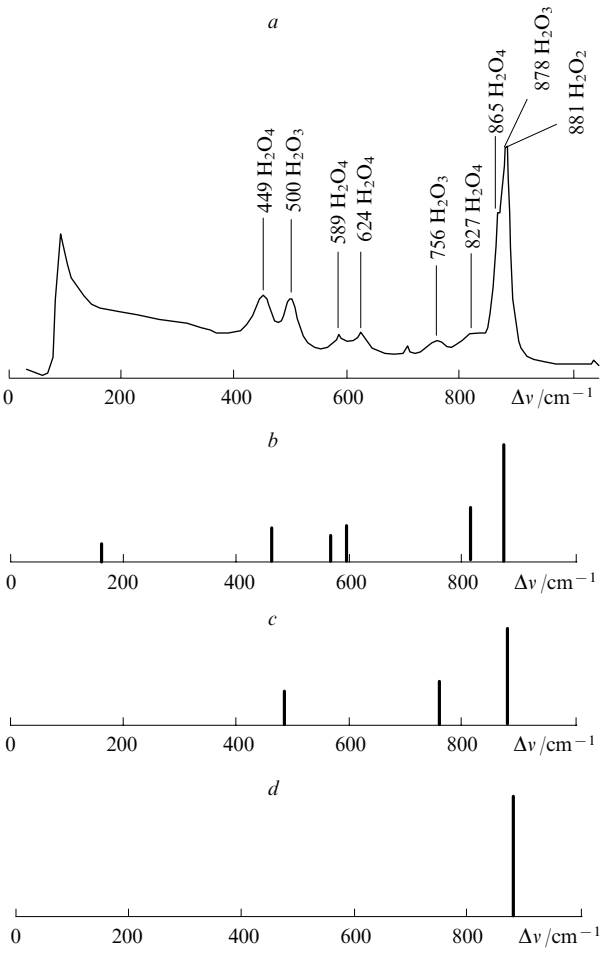


Figure 3. Experimental Raman spectrum of PRC (synthesized from 96.6 vol.% O_2 + 3.4 vol.% H_2) (*a*) and simulated spectra of H_2O_4 (*b*), H_2O_3 (*c*) and H_2O_2 (*d*) in the region of oxygen skeleton modes.[39]

IV. Chemical composition of peroxy radical condensates

The application of Raman spectroscopy and chemical analysis of decomposition products made it possible to reliably determine for the first time the composition of PRC obtained from electrically dissociated oxygen–hydrogen mixtures and water vapour or by the reaction of hydrogen with liquid ozone.

The quantitative contents of the major PRC components (H_2O, H_2O_2, H_2O_3 and H_2O_4) can be calculated from the numbers of moles of decomposition products ($N_{O_2}/N_{H_2O_2}$, N_{H_2O}) and relative intensities (I) of the most intense and well-resolved H_2O_4 and H_2O_3 lines at 449 and 500 cm^{-1} in the Raman spectra of the condensate. If the numbers of moles of components in the freshly prepared condensate are designated by $n(H_2O)$, $n(H_2O_2)$, $n(H_2O_3)$ and $n(H_2O_4)$, the following equations can be written:

$$n(H_2O) + n(H_2O_3) = N_{H_2O} \quad (6)$$

Table 2. Fundamental vibrational frequencies of the oxygen skeleton in H_2O_3 and H_2O_4 (cm^{-1}).

Approximate normal vibration type	Experiment			Calculation method				
	see [39]	see [47, 83 – 85]	see [33]	B3LYP/6-31 + G(d,p) (scaled) [39]	B3LYP/6-31 + G(d,p) (unscaled) [39]	B3LYP/6-311 + G(3df,2p) (see [23])	CCSD(T)/cc-pVTZ (see [23])	CCSD(T)-F12/cc-pVTZ-F12 (see [28])
Oxygen skeleton of H_2O_3								
OO symmetric stretching	878	~855	821.0	878	917	925	879	881
OO asymmetric stretching	756	755	776.3	760	795	795	784	774
OOO bending	500	500	509.1	486	508	516	508	511
Oxygen skeleton of H_2O_4								
OO symmetric stretching	865	~855	–	873	912	922	882	869
OO asymmetric stretching	827	~823	–	814	851	847	833	844
OO central stretching	624	~764	–	594	621	629	672	661
OOO bending 1	589	(435)	–	567	593	607	601	592
OOO bending 2	449	450	–	462	483	479	470	449
OOOO torsional	–	~98	–	162	169	172	166	159

Notes.

1. The descriptions of the types of H_2O_4 normal vibrations in Ref. 39 and in Refs 23, 28 and 47 somewhat differ.
2. The frequencies were taken from the final paper [47] based on experimental data reported in Refs 83 – 85. The reported [47, 83–85] spectra of H_2O_4 clearly show only peaks at 450 and ~823 cm^{-1}.
3. The H_2O_4 molecule was reported [10, 28] to have three stable conformations (isomers); the presented frequencies refer to isomer No. 3.[28]

$$n(H_2O_2) + n(H_2O_4) = N_{H_2O_2} \quad (7)$$

$$n(H_2O_3) + n(H_2O_4) = N_{O_2} \quad (8)$$

$$\frac{n(H_2O_4)}{n(H_2O_3)} = a\frac{I_{449}}{I_{500}} \quad (9)$$

The coefficient $a = 0.92$ was estimated from the intensities of Raman lines of hydrogen tri- and tetroxides, calculated by Levanov and co-workers,[39] taking account of the intensity ratio of the lines of analogous vibrations in the experimental Raman spectra of pure H_2S_4 and H_2S_3.[94] The presented relations form a non-degenerate system of four linear equations with four variables; solution of this system gives the numbers of moles of the major PRC components.

The compositions of the PRC obtained from electrically dissociated oxygen–hydrogen mixtures as a function of the composition of the initial gas mixture are shown in Fig. 4. When the oxygen content in the initial mixture is 60 vol.%–70 vol.%, the predominant components are H_2O_2 and H_2O_3. The highest fraction of H_2O_3 (30 mol.%) is attained when the gas fractions in the initial mixture are 70 vol.% O_2 and 30 vol.% H_2. As the initial oxygen fraction in the gas mixture further increases, the H_2O_3 and H_2O_2 contents in the condensate decrease, whereas the H_2O_4 and H_2O contents increase. The condensate prepared from 98 vol.% O_2 and 2 vol.% H_2 contains the highest amount of H_2O_4 (20 mol.%), while the major component of this condensate is water (55 mol.%).

Condensates synthesized from electrically dissociated water vapour were started to be studied in the 1930s. In most of the published works, H_2O_4 was considered to be the active component. Only in two papers,[68,84] there are data on the presence of hydrogen trioxide in this condensate. The $N_{O_2}/N_{H_2O_2}$ values for PRC obtained from water vapour are as follows: 0.11,[67] 0.13,[68] 0.15,[75] 0.11–0.17,[37] 0.15–0.17,[69] 0.16,[74] 0.16–0.18,[70] 0.17,[71] 0.18,[72] 0.2.[73] This value can approach unity in the case of effective cooling and minimization of the connecting channel length.[95,96]

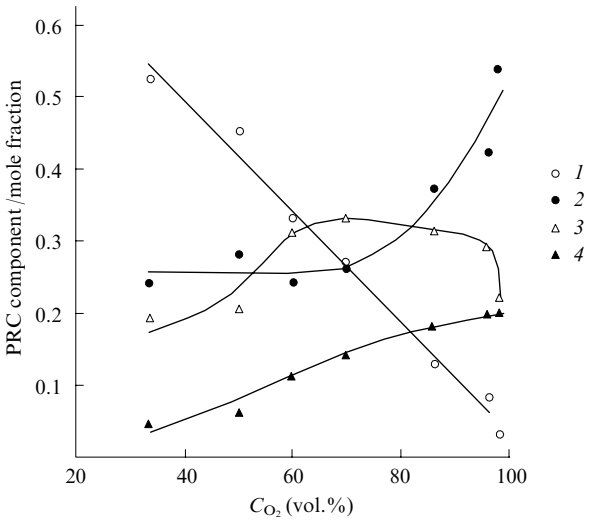


Figure 4. Variation of the PRC composition vs. oxygen content in the initial $H_2 + O_2$ gas mixture.[39]
Components: (*1*) H_2O_2, (*2*) H_2O, (*3*) H_2O_3, (*4*) H_2O_4.
Synthesis conditions: 1.5–5 h duration, 12 W rated power of the microwave discharge, 2.5 cm distance from the discharge to the synthesis zone, 3.2 litre h^{-1} flow rate, and ~0.9 mm Hg pressure in the reactor.

Modern investigations of PRC obtained from water vapour have been reported by Levanov *et al.*[37] In the Raman spectra of the condensates, characteristic signals of H_2O_3 with wave numbers of 500 and 756 cm^{-1} can be clearly seen. They are due to the OOO bending vibration and OO stretching vibration of the oxygen skeleton of this molecule. Hydrogen tetroxide gives rise to only one relatively weak and poorly resolved peak at 450 cm^{-1}, which was assigned to the OOO bending vibration 2. The most intense peak at 878 cm^{-1} is caused by superposition of lines of the OO symmetric stretching modes of hydrogen peroxide and trioxide. The analogous vibration in the case of hydrogen tetroxide is usually manifested as a shoulder (865 cm^{-1}) at this peak,[32,39] but it is not observed in the spectra of PRC prepared from water vapour. Thus, the amount of H_2O_4 is rather low, while H_2O, H_2O_2 and H_2O_3 are the major components. A quantitative estimate demonstrated that in most experiments,[37] the numbers of moles of PRC components formed from water vapour are in the approximate ratio $n(H_2O_2) : n(H_2O_3) : n(H_2O_4) \approx 50 : 7 : 1$.

It was found by Raman spectroscopy that on heating of the condensate, H_2O_4 is the first to decompose and H_2O_3 is the next; the final stage of decomposition of PRC components in the liquid phase involves decomposition of only H_2O_3.[37] This finding is important for interpretation of the results of calorimetric studies of PRC.[74,97,98]

The low-temperature condensate obtained by the reaction of hydrogen atoms with liquid ozone has the following characteristic feature: when particular experimental conditions are maintained, the $N_{O_2}/N_{H_2O_2}$ ratio is equal to unity and virtually does not depend on the time of treatment or concentration of hydrogen atoms in the gas phase.[49,50,77,80] Study of the magnetic susceptibility demonstrated the absence of occluded molecular oxygen in the freshly prepared $H^{\bullet}(g) - O_3(liq)$ condensate;[99] O_2 is formed only upon decomposition of the condensate on temperature rise. In view of these facts, it was suggested that the PRC formed in the $H^{\bullet}(g) - O_3(liq)$ system contains only hydrogen tetroxide and water.[50,99] However, the nature of active components was not elucidated.

Levanov *et al.*[32] investigated the condensate formed in the $H^{\bullet}(g) - O_3(liq)$ system by Raman spectroscopy. In the Raman spectrum, an intense peak is present with a maximum at 880 cm^{-1}. It is a superposition of three lines — 865, 878 and 881 cm^{-1} corresponding to the OO symmetric stretching modes of H_2O_4, H_2O_3 and H_2O_2 molecules, respectively.[39] The 878 and 881 cm^{-1} lines always coalesce, while the 865 cm^{-1} line is partly resolved, and in high-resolution spectra it is manifested as a shoulder at the main signal. These results make it possible to draw conclusions about the condensate composition and to verify whether the condensate actually consists of only hydrogen tetroxide and water.[50,99] If this was true, the spectrum would exhibit a single peak with a maximum at 865 cm^{-1}. Evidently, this is not the case: in the experimental spectra, the top of the peak is located at 879–880 cm^{-1}. The 865 cm^{-1} line is a shoulder with an intensity approximately twice lower than the intensity of the major signal. Hence, the condensate contains not only H_2O_4, but also H_2O_3 and H_2O_2. In view of the the fact that $N_{O_2}/N_{H_2O_2} \approx 1$ is characteristic of the

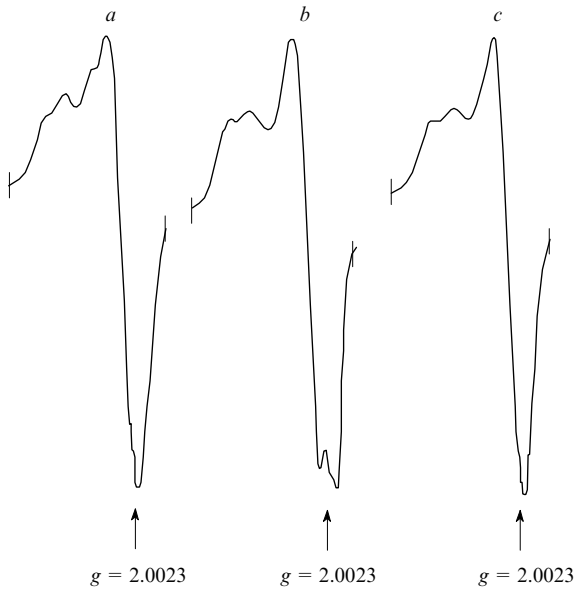


Figure 5. EPR spectra of the $HO_2^{\bullet}$ radicals in the PRC prepared from oxygen–hydrogen mixtures with O_2 content of 2–7 (*a*), 15–82 (*b*), 88–97 vol.% (*c*).[104]

condensate, one can conclude that the contents of H_2O_2 and H_2O_3 are equal. Thus, the condensate synthesized by the reaction of atomic hydrogen with liquid ozone contains not only hydrogen tetroxide and water, but also hydrogen trioxide and peroxide, with the amounts of H_2O_4, H_2O_3 and H_2O_2 being approximately equal.[32]

An important component present in PRC in small quantities is the $HO_2^{\bullet}$ free radical. This radical is responsible for the yellowish colour¶ and paramagnetism of freshly prepared condensates. According to EPR study of PRC,[54, 100, 101] the concentration of $HO_2^{\bullet}$ radicals is 0.3 mass % – 0.5 mass % and virtually does not depend on the conditions of synthesis. Typical EPR spectra of the $HO_2^{\bullet}$ radical in the PRC matrix are shown in Fig. 5. In low fields (*g*-factor $\approx$ 4), the EPR spectrum exhibits a weak signal for the $HO_2^{\bullet} \cdots HO_2^{\bullet}$ radical pair.[101]

In the reaction of $H^{\bullet}$ and O_2, the $HO_2^{\bullet}$ radicals are generated on the surface of the growing condensate (in the quasi-liquid layer) rather than in the gas phase.[102, 103] In this case, most of the radicals are spent for the formation of the major condensate components, and only a minor fraction of $HO_2^{\bullet}$ has no time to react and is stabilized in the PRC matrix. For short times of freezing (thin film of PRC), the accumulation of $HO_2^{\bullet}$ is linear, irrespective of the experimental conditions; this is indicative of a constant temperature of the growing condensate surface. As the time of freezing increases, the accumulation rate decreases and deviations from the linearity appear, because of increasing temperature of the condensate surface following the increase in its amount during the synthesis.[102, 103]

The kinetics of PRC decomposition has been investigated by EPR spectroscopy.[101, 104] Recombination of the $HO_2^{\bullet}$ radicals starts at 90 K and ends at 153 K, *i.e.*, by the onset of decomposition of the major PRC components (155 K), there are no radicals left. In view of the virtual absence of gas evolution during PRC heating up to a temperature of 153 K and considering the published data on the magnetic susceptibility of PRC,[99] the recombination of $HO_2^{\bullet}$ radicals in the indicated temperature range is concluded to give H_2O_4. The $HO_2^{\bullet}$ decay is stepwise: at this temperature, only a certain fraction of radicals disappears and the kinetic curve reaches saturation. A diffusion model has been proposed for $HO_2^{\bullet}$ radical recombination in PRC, describing the stepwise recombination and suitable for determining the diffusion coefficient in a low-temperature matrix.[105]

Using a model that implies an activation energy (E_a) distribution, the activation energies of radical recombination reactions were determined.[101, 104] The characteristic E_a values are $\sim$10 (90–130 K) and $\sim$20 kcal mol^{-1} (130–145 K).[101] They considerably exceed the apparent activation energy for the $HO_2^{\bullet}$ recombination in the gas phase and are caused by the low mobility of radicals in the low-temperature matrix. It was suggested[101, 104] that diffusion in the amorphous condensate is the only rate-limiting stage at 90–130 K, while at 130–145 K, the diffusion is additionally hampered by the onset of the phase transition — crystallization of the condensate, which takes place at 153–163 K.[106–108]

V. Mechanism of formation of hydrogen polyoxides and kinetic model of the synthesis of peroxy radical condensates

The composition of peroxy radical condensates is completely dictated by and depends, in a complex manner, on the composition of the gas phase occurring in contact with the cold surface on which the PRC is formed. Detailed EPR investigations of the gas phase composition during experiments on PRC synthesis have been reported.[109–114] The oxygen–hydrogen mixtures were dissociated into atoms in high-frequency or microwave glow discharge, the cavity of the EPR spectrometer was arranged at the end of the connecting channel at some distance from the discharge. In some cases, the zone of PRC synthesis was inside the cavity.[113, 114] The EPR measurements showed the presence of the $H^{\bullet}$ and $^{\bullet}O^{\bullet}$ atoms, $HO^{\bullet}$ radicals and O_2 molecules. Typical dependences of the concentrations (*C*) of these species on the composition of the initial gas mixture are shown in Fig. 6. The highest concentration of $HO^{\bullet}$ is approximately two orders of magnitude lower than the highest concentrations of $H^{\bullet}$ and $^{\bullet}O^{\bullet}$.

The atoms and radicals that exist directly in the discharge area can be detected by emission spectroscopy. The discharge emission spectra of oxygen–hydrogen mixtures exhibit intense lines of the excited $H^{\bullet}$ and $^{\bullet}O^{\bullet}$ atoms, the relative concentrations of which are shown in Fig. 7. The intensities of other lines are two to three orders of magnitude lower (their nature was not studied).

The full composition of the gas phase was determined by mathematical modelling of the chemical reaction kinetics in the connecting channel.[110, 113, 115] The set of the considered chemical reactions mainly described the well-known chain mechanism of the reaction between hydrogen and oxygen. At low pressure ($\sim$1 mm Hg), considerable role is played by the decay of the $H^{\bullet}$ and $^{\bullet}O^{\bullet}$ atoms and the $HO^{\bullet}$ radicals on the connecting channel wall. From the results of experimen-

¶ The peroxy radical condensates synthesized by the reaction $H^{\bullet}(g) + O_3(liq)$ are light-blue- or blue-coloured due to residual ozone.

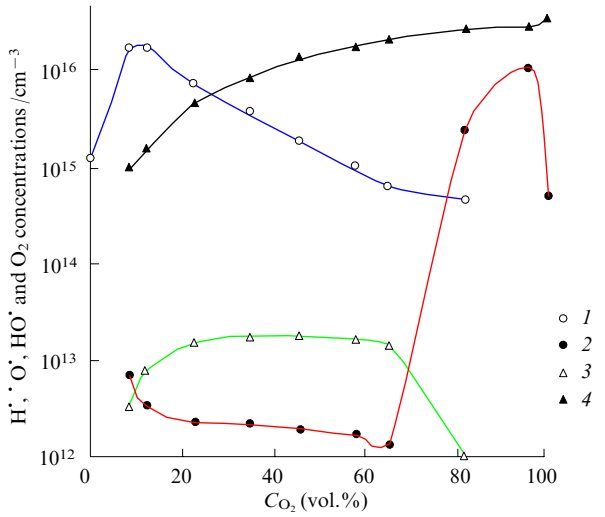


Figure 6. Variation of the concentrations of H• (*1*), •O• (*2*), HO• (*3*) and O_2 (*4*) at a 16 cm distance from the microwave discharge (20 W rated power) in an $H_2 + O_2$ mixture *vs.* initial composition of the gas mixture at a 0.7 litre h^{-1} flow rate and a reactor pressure of 1 mm Hg.[113]

tal determination of the concentrations of H•, O•, HO• and O_2 and modelling of the kinetics of reactions in the connecting channel, it was ascertained that water is the only PRC component that can be formed in the gas phase and then freeze out on a cold surface. The concentrations of the other possible components, in particular, H_2O_2, $HO_2^•$ and O_3, in the gas phase are too low to explain the presence of these components in the condensates. Hence, all PRC components, apart from water, are formed only in chemical reactions on the surface of the growing condensate.

In order to find out what particular atoms, radicals or molecules present in the gas phase can serve as initial species for low-temperature synthesis of PRC components, Levanov *et al.*[115] compared the concentrations of gas-phase species (determined from experimental EPR spectroscopy and mathematical modelling data) and yields of low-temperature condensation products under similar conditions (the data of Refs 59 and 116). From the results,[115] one can draw the important conclusion that three species coming from the gas phase act as reactants in the low-temperature synthesis from dissociated $H_2 + O_2$ mixtures or from water and hydrogen peroxide vapours, namely, hydrogen and oxygen atoms (H• and •O•) and molecular oxygen. It should be borne in mind that the •O• atom in the gas phase is highly reactive compared with H• or O_2. Therefore, even a minor dissimilarity of experimental conditions in the synthesis of PRC and in determination of the gas phase composition may lead to a significant underestimation of the real concentration of •O• near the synthesis zone.

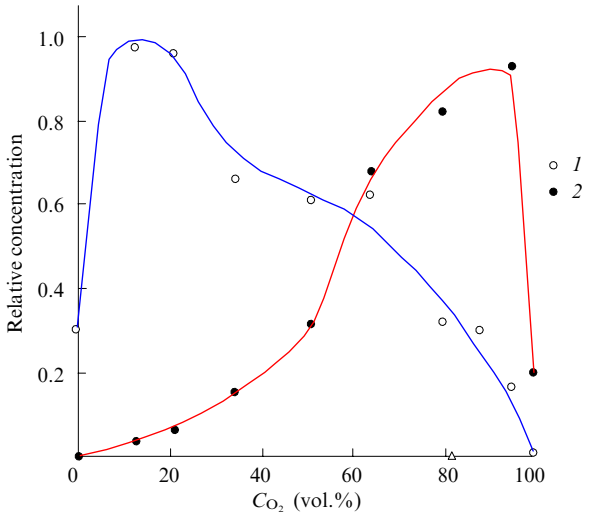


Figure 7. Variation of the relative concentrations of H• (*1*) and •O• (*2*) atoms in the microwave discharge plasma (12 W rated power) in an $H_2 + O_2$ mixture *vs.* initial composition of the gas mixture at a 3.2 litre h^{-1} flow rate and 0.8 mm Hg reactor pressure.

In non-equilibrium electric discharges, which are used in PRC synthesis, there are free electrons, but their reactions can be neglected. Indeed, PRC can arise both upon direct contact of the electric discharge plasma with a cold surface and upon reactions of atoms and radicals drawn out of the discharge; in the latter case, the concentration of electrons is negligibly low compared with their concentration in the discharge. However, in both cases, condensates with similar properties are formed. Due to very high reactivity, electrons are usually rapidly consumed in direct or mediated reactions with positively charged ions and do not migrate from the discharge plasma to the condensed phase. This is confirmed, for example, by the fact that, among other methods, hydrogen atoms can be generated in a liquid solution by a high-frequency electric discharge in a flow of hydrogen gas, which is then vigorously mixed with the solution.[117] This process is not considered as a source of electrons (the only method for generating free electrons in an aqueous solution is water radiolysis).[117] In addition, analysis of the relevant literature provides the conclusion that under experimental conditions of PRC synthesis, the concentration of electrons in the gas phase is insufficient for the formation of hydrogen polyoxides.

To account for the observed yields of polyoxides, the concentration of the initial gas-phase species should exceed $\sim 10^{13} - 10^{14}$ cm^{-3} (if reactions of one species lead to the formation of one polyoxide molecule).[115] The concentrations of electrons in the discharges similar to those used for PRC synthesis are $< 3 \times 10^{10}$ cm^{-3} (in a direct current glow discharge plasma in oxygen)[118] and they are several orders of magnitude lower in the afterglow. While modelling the kinetics of ozone formation in oxygen discharge plasma, Chang and Masuda[119] concluded that at temperatures <170 K, reactions involving electrons or ions do not contribute to the formation (decay) of ozone molecules. This referred to ozone formation particularly in the discharge plasma in the gas phase, in which electrons are present and play a crucial role in dissociation of molecules into atoms, rather than to ozone formation upon low-temperature condensation.

A very important issue is the mechanism of low-temperature PRC synthesis and formation of hydrogen polyoxides as PRC components. Indeed, it is of interest how relatively long chain molecules of polyoxides are formed from the small $H-O-O_2$, or $H-O_3$ species. In many early papers starting from the 1930s (see discussions[39,45,120]), various possible mechanisms have already been proposed for this reaction. However, all of them were suitable only for

qualitative description of some limited set of experimental results. Furthermore, strictly speaking, the PRC composition was unknown at that time (it was ultimately established only recently [32, 37, 39]); therefore, the task of constructing a detailed mechanism (taking into account as fully as possible the significant chemical reactions and estimation of their rate constants) and a quantitative kinetic model could not be even put forward, because of the lack of the required initial data.

The mechanism of formation of hydrogen polyoxides in the reaction system comprising gas-phase hydrogen atoms and liquid ozone is especially important owing to the unique properties of the resulting condensate. The $H^{\bullet}(g) + O_3(liq)$ condensate contains hydrogen peroxide, the polyoxides H_2O_3 and H_2O_4 in comparable amounts and water, the value $N_{O_2}/N_{H_2O_2}$ being equal to unity and virtually independent of the treatment time or concentration of hydrogen atoms in the gas phase.[49, 50, 77, 80] This indicates that the concentrations of H_2O_2 and H_2O_3 in the condensate are equal for some reason. In addition, it is known that PRC is a solid glass-like material in which hydrogen polyoxides are stabilized. Meanwhile, the synthesis of hydrogen polyoxides by the reaction $H^{\bullet}(g) + O_3(liq)$ takes place only if a liquid ozone layer is present on the cooled surface;[121] when the $H^{\bullet}$ atoms react with solid ozone, H_2O_4 and H_2O_3 are not formed. The mechanism and the corresponding model of PRC synthesis should account for all these peculiarities.

The quantitative kinetic model of PRC synthesis was constructed proceeding from the following views.[32] The liquid ozone layer located on the cold surface ($T = 77$ K) is bombarded by hydrogen atoms coming from the gas phase. All chemical reactions occur in the liquid phase. The primary step is the reaction of $H^{\bullet}$ and O_3(liq); the $HO^{\bullet}$ and $HO_2^{\bullet}$ radicals are generated in the subsequent reactions involving O_3. The active components of the condensate, H_2O_4, H_2O_3 and H_2O_2, are generated in diffusion-controlled reactions between the $HO^{\bullet}$ and $HO_2^{\bullet}$ radicals proceeding without a barrier. Water is the product of reaction between the $HO^{\bullet}$ radical and the H_2O_4, H_2O_3 and H_2O_2 molecules. The H_2O, H_2O_2, H_2O_3 and H_2O_4 molecules formed in the liquid ozone layer diffuse towards the cold surface and form a solid phase layer on the surface. The molecules located in the solid phase are stabilized and inaccessible for any chemical transformations.

On the basis of analysis of published data on the kinetics and mechanism of the relevant elementary reactions, the following reactions were proposed to occur in the liquid phase at 77 K:

$$H^{\bullet} + O_3 \longrightarrow HO^{\bullet} + O_2 \quad (10)$$

$$HO^{\bullet} + O_3 \longrightarrow HO_2^{\bullet} + O_2 \quad (11)$$

$$HO_2^{\bullet} + O_3 \longrightarrow HO^{\bullet} + 2O_2 \quad (12)$$

$$H^{\bullet} + O_2 \longrightarrow HO_2^{\bullet} \quad (13)$$

$$H^{\bullet} + HO^{\bullet} \longrightarrow H_2O \quad (14)$$

$$H^{\bullet} + HO_2^{\bullet} \longrightarrow H_2O_2 \quad (15)$$

$$HO^{\bullet} + HO^{\bullet} \longrightarrow H_2O_2 \quad (16)$$

$$HO^{\bullet} + HO_2^{\bullet} \longrightarrow H_2O_3 \quad (17)$$

$$HO_2^{\bullet} + HO_2^{\bullet} \longrightarrow H_2O_4 \quad (18)$$

$$HO^{\bullet} + H_2O_2 \longrightarrow H_2O + HO_2^{\bullet} \quad (19)$$

$$HO^{\bullet} + H_2O_3 \longrightarrow H_2O + HO^{\bullet} + O_2 \quad (20)$$

$$HO^{\bullet} + H_2O_4 \longrightarrow H_2O + HO_2^{\bullet} + O_2 \quad (21)$$

The reactions of transition to the solid phase are described by quasi-chemical equations

$$H_2O \longrightarrow H_2O(s) \quad (22)$$

$$H_2O_2 \longrightarrow H_2O_2(s) \quad (23)$$

$$H_2O_3 \longrightarrow H_2O_3(s) \quad (24)$$

$$H_2O_4 \longrightarrow H_2O_4(s) \quad (25)$$

The primary reaction in the liquid phase is the reaction of the hydrogen atom with the ozone molecule. This reaction gives the hydroxyl radical and molecular oxygen, with the mechanism including the intermediate formation of $HO_3^{\bullet}$ (Refs 122–125).

$$H^{\bullet} + O_3 \longrightarrow HO_3^{\bullet} \longrightarrow HO^{\bullet} + O_2 \quad (26)$$

The $HO_3^{\bullet}$ radical is very unstable and easily decomposes to $HO^{\bullet}$ and O_2.[126] Therefore, the $HO_3^{\bullet}$ species is not considered in the model and the reaction of $H^{\bullet}$ with O_3 is written as equation (10).

Reaction (10) is very fast: according to quantum chemical calculations, the reaction rate is fairly high even at 77 K.[122] The subsequent chemical reactions include the reaction of the $HO^{\bullet}$ and $HO_2^{\bullet}$ radicals with ozone according to equations (11) and (12). The rates of these reactions at low temperature are discussed below.

As a result of reactions (10)–(12), the $HO^{\bullet}$ and $HO_2^{\bullet}$ free radicals and O_2 molecules are formed in liquid ozone. These radicals and hydrogen atoms can react according to equations (13)–(18). The activation barriers of these reactions are almost zero and the rate of formation of the reaction products is determined by the dissipation dynamics of the excess energy of the reactants. In the liquid phase, these reactions are diffusion-controlled. In the case of low temperatures, this statement was confirmed experimentally in relation to the reaction [127]

$$^{\bullet}O^{\bullet} + O_2 \longrightarrow O_3 \quad (27)$$

The hydrogen atoms and $HO^{\bullet}$ radicals present in the liquid phase are active species and can, in principle, react with the H_2O_2, H_2O_3 and H_2O_4 molecules. Extrapolation of the experimental and theoretical data [128–130] on the rate constants of gas-phase reactions

$$H^{\bullet} + H_2O_2 \longrightarrow H_2 + HO_2^{\bullet} \quad (28)$$

$$H^{\bullet} + H_2O_2 \longrightarrow HO^{\bullet} + H_2O \quad (29)$$

to the temperature of 77 K prompts the conclusion that the reactions of hydrogen atoms with hydrogen peroxide and with structurally related hydrogen tri- and tetroxides can be neglected.

Meanwhile, the reactions of the hydroxyl radical with the H_2O_2, H_2O_3 and H_2O_4 molecules should be included in the model. Indeed, the rate constant of reaction (19) increases as the temperature is decreased from 296 to 96 K; at 96 K, it is very high — 1.2×10^{-11} cm^3 molecule^{-1} s^{-1} (Ref. 131). This temperature dependence is due to the formation of the complex $HO^{\bullet} \cdots H_2O_2$, which is more stable at low temperature.[132, 133] The products are

formed as a result of hydrogen atom transfer in the complex by the tunnelling mechanism. The reactions of $HO^{\bullet}$ with H_2O_3 and H_2O_4 have not been studied. In our opinion, these reactions are similar to reaction (19); they are described by equations (20) and (21) and their rate constants coincide with that of reaction (19) in the order of magnitude.

With the assumptions made, reactions (10)–(21) reflect the whole set of chemical transformations that occur in the liquid phase during PRC synthesis. It has been shown [32] that the numerical values for the rate constants of reactions (10) and (13)–(21) can be estimated from the Smoluchowski equation [134, 135] for diffusion-controlled processes.

Reactions (11) and (12) are slower than (10) and (13)–(21). The rate constant of gas-phase reaction (12) follows an abnormal temperature dependence. It decreases with decreasing temperature and tends to a limiting value of $\sim 10^{-15}$ cm^3 molecule^{-1} s^{-1} (Refs 136 and 137); this value can be used as an estimate for the rate constant of reaction (12) in the liquid phase in the system $H^{\bullet}(g)-O_3(liq)$.

The experimental and calculated data on the rate constant for reaction (11) do not allow unambiguous estimation of this constant at low temperature. The extrapolation of the temperature dependences reported in two papers [138, 139] leads to the values of $\sim 10^{-15}$ and 10^{-17} cm^3 molecule^{-1} s^{-1}, respectively, at 77 K. Therefore, in the model, the calculations are carried out for various rate constant values in the range of $10^{-17}-10^{-15}$ cm^3 molecule^{-1} s^{-1}.

The concentrations of ozone and molecular oxygen in the liquid phase were estimated using the densities of liquid ozone and O_3-O_2 solutions reported in two publications.[140, 141]

Some model parameters could not be reliably estimated on the basis of published sources, *i.e.*, they were uncertain. For example, this refers to the specific rates of quasi-chemical reactions (22)–(25), which describe the transfer of the major PRC components from the liquid to the solid phase. Second, this refers to the Hertz–Knudsen equation parameters (gas-phase concentration of the $H^{\bullet}$ atoms and the surface area to volume ratio of the liquid ozone layer), which describe the rate of arrival of $H^{\bullet}$ atoms from the gas phase to the liquid ozone layer. In calculations, the uncertain parameters were varied over broad ranges definitely covering their possible values.

According to the accepted model of PRC formation, the liquid phase is an open system which receives a steady-state flow of hydrogen atoms from the gas phase. The H_2O_4, H_2O_3, H_2O_2 and H_2O molecules formed in reactions (10)–(21) migrate to the solid phase at a constant specific rate. The concentration of ozone (and also molecular oxygen if the O_3-O_2 azeotrope is used) in the liquid phase remains constant during the synthesis, but the volume of the liquid phase decreases. Hence, a steady-state regime is established in which the formation and consumption rates of the intermediates, $H^{\bullet}$, $HO^{\bullet}$, $HO_2^{\bullet}$, H_2O, H_2O_2, H_2O_3 and H_2O_4, in the liquid phase are equal and their concentrations are time-independent. Therefore, the concentrations of the above-mentioned intermediates and the rates of formation of components of the solid condensate can be calculated by solving a system of algebraic equations corresponding to the chemical kinetics differential equations for reactions (10)–(25) in the steady-state case.

The results of calculations according to this model were in excellent agreement with the whole set of experimental data on the composition and properties of PRC in the $H^{\bullet}(g)-O_3(liq)$ system. In particular, the calculated $N_{O_2}/N_{H_2O_2}$ ratios virtually did not depend on the uncertain model parameters and were in the range of 0.97–1.03. This means that the key feature of the condensate in the $H^{\bullet}(g)+O_3(liq)$ system — the $N_{O_2}/N_{H_2O_2}$ ratio equal to unity irrespective of experimental factors — is reproduced very well.[49, 50, 77, 80] The calculated mole fractions of condensate components, H_2O_4, H_2O_3 and H_2O_2, confirm the experimental result, according to which these values in a real condensate are approximately equal.

The mechanisms of reactions (10)–(25) and the model are in agreement with the observation that the reaction of hydrogen atoms with solid ozone affords only water and hydrogen peroxide,[142, 143] whereas the polyoxides H_2O_3 and H_2O_4 cannot be obtained.[121] Indeed, bombardment of solid ozone with hydrogen atoms gives rise to the $HO^{\bullet}$ and $HO_2^{\bullet}$ radicals by reactions (10)–(12). The solid-phase diffusion is slow; therefore, these radicals are relatively immobile. As a result, they only react with the $H^{\bullet}$ atoms from the gas phase according to equations (14) and (15) to give H_2O and H_2O_2, whereas reactions (17) and (18), giving rise to H_2O_3 and H_2O_4, are almost impossible.

A model of PRC synthesis in the $H^{\bullet}(g)-O_2(g)$ system has been constructed [144] using an approach similar to that chosen above for the $H^{\bullet}(g)+O_3(liq)$ system. The initial reactants are $H^{\bullet}$ atoms and the O_2 molecules coming from the gas phase, the flow of these species being relatively intense. A liquid (quasi-liquid) layer, in which the synthesis of PRC components takes place, is formed near the cold surface. This layer is composed of the adsorbed reactants and the products of reactions initiated by the primary interaction $H^{\bullet}+O_2$. The existence of this layer in the liquid state is maintained by heat evolution as a result of chemical reactions and dissipation of the energy of gas-phase species. The hydrogen polyoxide molecules formed upon the reactions in the liquid layer can migrate to the solid phase that directly adjoins the cooled surface and be stabilized there. The solid condensate is thus formed.

In the liquid layer, the primary reaction is the reaction between the $H^{\bullet}$ atoms and the O_2 molecule to give the $HO_2^{\bullet}$ radical. This is followed by reactions (15) and (18) yielding condensate components. Reactions (13), (15) and (18) are diffusion-controlled, their rate constants being determined by the Smoluchowski equation. The $H^{\bullet}$ atoms and the $HO_2^{\bullet}$ radicals are highly reactive species; therefore, they can be considered to be almost completely consumed in fast reactions (13), (15) and (18) in the liquid layer. The H_2O_2 and H_2O_4 molecules are much more inert. They are formed in reactions (15) and (18) and migrate to the solid phase, thus forming the desired PRC. The migration processes from the liquid to solid phase are described by quasi-chemical equations (23) and (25). Thus, in the $H^{\bullet}(g)-O_2(g)$ system, the formation of PRC components is described by diffusion-controlled chemical reactions (13), (15) and (18) in the liquid layer and processes of migration to the solid phase (23) and (25).

At low temperature, the components of solid PRC are virtually inaccessible for any chemical reactions. This was confirmed by Nekrasov *et al.*,[145, 146] who demonstrated that hydrogen peroxide as a part of solid $H_2O_2-H_2O$ condensates does not react with hydrogen atoms that come from the gas phase.

Proceeding from the condition of stationary concentrations of $HO_2^{\bullet}$, H_2O_2 and H_2O_4, a theoretical expression was obtained for the $N_{O_2}/N_{H_2O_2}$ ratio for the PRC synthesized by the reaction between $H^{\bullet}$ and O_2,[144]

$$\frac{N_{O_2}}{N_{H_2O_2}} = 1 - 4\left[3 + \left(1 + \frac{\sqrt{2}C_{O_2}}{C_{H^\bullet}}\right)^{1/2}\right]^{-1} \quad (30)$$

where $C_{H^\bullet}$ and C_{O_2} are the $H^\bullet$ and O_2 concentrations in the gas phase, respectively. Assumptions were made that the rate constants for diffusion-controlled reactions (13), (15) and (18) are approximately equal and that the $H^\bullet$ and O_2 concentration ratio in the liquid layer is equal to the ratio of flow rates of these species from the gas to liquid phase.

Attention is attracted by the fact that theoretical equation (30) reproduces very well the available experimental results on the properties of PRC formed in the $H^\bullet(g) - O_2(g)$ system from publications of different authors[60–62] who used different experimental conditions (reactor designs, cooling medium temperatures and total pressures; the presence of admixtures of other gases). This confirms the validity of the PRC formation model we discuss.

In reality, the set of physicochemical transformations that occur during the PRC synthesis by the reaction $H^\bullet + O_2$ is more complex than it is assumed in the model. The PRC decomposition products usually contain considerable amounts of water rather than only hydrogen peroxide and molecular oxygen, as would follow from the mechanism described by reactions (13), (15), (18), (23) and (25). Water is formed, as a rule, in oxygen–hydrogen cycle reactions in the gas phase or on the surface of the inlet parts of the reactor rather than in the liquid layer. These processes are initiated by the reaction between $H^\bullet$ and O_2 and are possible if the atomic hydrogen and molecular oxygen are brought in contact before they enter the low-temperature liquid layer (for reactions in gas phase, see Ref. 115). In the ideal case, only $H^\bullet$ and O_2 come from the gas phase and all chemical reactions — reactions (13), (15) and (18) — proceed in the low-temperature liquid layer. Then the condensate is expected to consist of only hydrogen peroxide and tetroxide, while the liquid phase formed upon its decomposition would be 100% hydrogen peroxide. This case has been implemented:[60] the products of decomposition of the condensate synthesized by the reaction of $H^\bullet$ atoms with an excess of O_2 at 4.2 K contained very little water and consisted almost entirely of pure hydrogen peroxide and molecular oxygen.

No quantitative kinetic model has yet been developed for the synthesis of PRC from electrically dissociated oxygen–hydrogen mixtures. Unlike the systems considered above, a $H_2 + O_2$ mixture, after the electric discharge, contains significant concentrations of not only $H^\bullet$ atoms and O_2 molecules, but also $^\bullet O^\bullet$ atoms. Therefore, apart from reactions (10)–(25), low-temperature reactions of oxygen atoms should also be taken into account for considering the PRC synthesis in atomized oxygen–hydrogen mixtures. Extrapolation of the experimental rate constants of the reactions of $^\bullet O^\bullet$ with H_2O and H_2O_2 (Refs 147 and 148) to the temperature corresponding to PRC synthesis has shown that these reactions can be neglected. It is also possible to neglect the reactions of the $^\bullet O^\bullet$ atoms with the H_2O_3 and H_2O_4 molecules, similar to H_2O_2. Meanwhile, the reaction

$$^\bullet O^\bullet + HO_2 \longrightarrow HO^\bullet + O_2 \quad (31)$$

must be included, because according to quantum chemical calculations,[149,150] the rate constant of this reaction in the gas phase at 77 K is comparable with the diffusion limit in the liquid phase. The important contribution of this reaction is confirmed by the increase in proportion of water in the condensate with increasing concentration of the $^\bullet O^\bullet$ atoms in the gas phase (the gas-phase concentration of O_2 molecules simultaneously increases, while the $H^\bullet$ and H_2 concentrations decrease). It may seem that the proportion of water should, conversely, decrease, since the H_2O molecule contains the highest amount of hydrogen among other condensate components. However, it has been found[32] that the key pathway to water in the PRC is the reaction of the $HO^\bullet$ radical with other components — H_2O_2, H_2O_3 and H_2O_4 — according to equations (19)–(21). Reaction (31) is a significant source of $HO^\bullet$ radicals for these reactions; the rate of $HO^\bullet$ formation *via* other reactions is low. In oxygen-enriched mixtures, it is also necessary to consider the formation of ozone by reaction (27), the kinetics of which at low temperature has been experimentally studied.[127] The set of reactions (10)–(31) is sufficient to interpret the formation of the major PRC components (H_2O, H_2O_2, H_2O_3, H_2O_4) in atomized oxygen–hydrogen systems. Preliminary estimates have shown that a quantitative kinetic model of PRC synthesis could be based on these reactions.

Thus, Levanov *et al.*[32,144] proposed for the first time a detailed mechanism and a quantitative kinetic model of PRC synthesis and formation of hydrogen polyoxides *via* low-temperature condensation of dissociated oxygen–hydrogen systems; these results can serve for interpretation and prediction of the composition and properties of low-temperature condensates in the $H^\bullet(g) + O_3(liq)$ and $H^\bullet(g) + O_2(g)$ systems at a quantitative level, while at a qualitative level, they are suitable for describing the PRC composition in all known oxygen–hydrogen systems. This model provides a plausible interpretation for the formation of relatively complex molecules, HOOOOH and HOOOH, from simple species, $H^\bullet$, $^\bullet O^\bullet$ and O_2, particularly, under conditions of PRC synthesis and gives an understanding of why under other similar conditions (reactions of $H^\bullet$ atoms with solid ozone or oxygen, matrix isolation experiments), the formation of hydrogen polyoxides is virtually impossible. Apparently, this model is not only the first quantitative model of PRC synthesis, but generally the first quantitative model for kinetics of complex chemical reactions in a liquid medium at low ($\sim$77 K) temperatures.

VI. Decomposition kinetics of peroxy radical condensates

The peroxy radical condensates are stable only at low temperatures, while on heating to room temperature, they completely decompose. The decomposition kinetics and the physical transformations of PRC on heating have been addressed by many researchers since the 1940s. In most experiments, decomposition was monitored by measuring the increase in the pressure of the gaseous product — molecular oxygen.

The temperatures of the onset of decomposition and physical transitions taking place on heating of condensates of various compositions reported by different authors are in good agreement (Table 3). The characteristic temperatures are as follows: onset of decomposition, 153–163 K; crystallization, 158–163 K; melting, 203–212 K. The onset of decomposition is accompanied by crystallization of the condensate. These data are confirmed by the results of X-ray and electron diffraction studies, which are discussed below. The transparent condensate is covered with cracks and then sharply grows in size and looks like snow. In the

Table 3. Temperatures (K) of the onset of decomposition and phase transformations of PRC.

Methods of synthesis	Onset of decomposition	Crystallization	Melting	Ref.
H + O_2(g)	153 – 163	158 – 173	212	62, 65, 108, 151
H + O_3(g)	153 – 158	–	–	48, 61
H + O_3(liq)	153 – 165	158	203 – 208	49, 50, 77, 80, 107
H + H_2O_2(g)	160	160	–	106
H_2O_2 (dissociation)	153	–	–	76
H_2O (dissociation)	153 – 165	158 – 165	203 – 212	68, 74, 75, 77, 97, 107, 108, 151 – 153

PRC synthesized at ~77 K, the $HO_2^{\bullet}$ free radicals (0.3 mass % – 0.5 mass %) are stabilized.[100, 101] They undergo recombination and decay in the 90 – 153 K temperature range, prior to the decomposition of the major components.[101, 104]

Meanwhile, the kinetic characteristics of PRC decomposition stages are substantially scattered, which is due to both human (imperfection of the procedures for processing and analysis of experimental gas evolution curves in early studies) and objective factors (complex chemical and phase compositions of the condensate depending on particular experimental conditions). It is known that water, which is a major PRC component, forms a solid amorphous phase upon condensation on a surface with a temperature of 77 K, the properties of this phase being dependent on the deposition conditions. On heating, it is first transformed into cubic ice at a temperature of ~150 K and then into hexagonal ice in the range of ~200 – 220 K.[154] Frozen hydrogen peroxide solutions can also exist in the amorphous state at low temperature (77 K); they crystallize at 161 – 165 K.[108, 155] Phase transitions occur in the PRC simultaneously with chemical reactions of decomposition of active components and can considerably affect the reaction kinetics.

It is noteworthy that amorphous ice can absorb considerable amounts of gases and then release them on heating.[154, 156, 157] However, the content of occluded gases (O_2 or H_2) in PRC is very low and they barely make any contribution to gas evolution during decomposition. The occluded oxygen in the condensate could be detected by Raman and EPR spectroscopy. The single peak of occluded oxygen has a wave number of 1552 cm^{-1}; in the Raman spectra of the condensates, this peak is weak or absent.[32, 37, 39] Gromov *et al.*[158] were able to record the EPR line *E* of oxygen located in the PRC cavities in the beginning of decomposition of active components, whereas the EPR spectra of freshly prepared condensates show the absence of O_2.

In early publications,[75, 151] two stages of PRC decomposition were found and their activation energies were determined. The temperature ranges of the stages are as follows: 158 – 215 and 215 – 238 K;[75] and 158 – 212 and 212 – 243 K.[151]

In more thorough studies of the isothermal and non-isothermal decomposition, with graphical differentiation being used for the processing of experimental curves, three stages for PRC decomposition were identified.[54] In a study of the condensate decomposition,[159] the experimental conditions (the reactor size and the heating rate) were chosen in such a way as to rule out the effect of process heats on the kinetic parameters. It was found that decomposition occurs in three stages. This research was continued by Gromov *et al.*,[158] who confirmed three stages of gas evolution. Furthermore, decomposition of PRC synthesized from a hydrogen – oxygen mixture with abnormally high content of oxygen (97 vol.%) was studied.[158] This condensate completely decomposed within the first two stages, with their temperature ranges being the same as indicated in Table 4, which summarizes characteristics of gas evolution stages during decomposition of PRC according to the results of above-mentioned extensive and thorough studies.[54, 158, 159]

The question of what particular active components of PRC decompose during each gas evolution stage deserves keen attention. According to recent data,[32, 37, 39] this issue was not solved in the studies reported before 2000, because the composition of the condensates was not reliably elucidated. For example, it was believed[158, 159] that the final stage includes degradation of hydrogen tetroxide in the liquid solution and evolution of dissolved oxygen.[158] Note that some early experimental studies on PRC (see, for example[74, 97 – 100]) are of considerable value. However, the drawn conclusions have to be corrected, because the PRC composition was unknown at that time. The conclusions of other studies, in particular, those addressing the decomposition kinetics,[68, 75] are also to be revised.

Studies of PRC decomposition by Raman spectroscopy have shown[37, 39] that on heating of the solid condensate at temperatures below the melting point, the intensities of the signals for both hydrogen trioxide and tetroxide decrease, with the H_2O_4 peaks disappearing much faster. In the molten condensate, only H_2O_3 is left. Thus, the final stage

Table 4. Characteristics of gas evolution stages in PRC decomposition.[54, 158, 159]

Stage	*T*/K	E_a/kcal mol^{-1}	Ref.
Peroxy radical condensates obtained from water vapour			
1	163 – 178	18.4	54
2	178 – 203	9.2	54
3	203 – 250	9.2	54
Peroxy radical condensates obtained from $H_2 + O_2$ *mixtures of various compositions*			
1	155 – 165	34	159
2	170 – 190	12	159
3	195 – 225	12	159
1	150 – 170	–	158
2	170 – 200	–	158
3	200 – 215	–	158

corresponds to decomposition of hydrogen trioxide in a molten condensate, that is, a liquid solution mainly composed of water and hydrogen peroxide.

In view of the whole set of experimental data, the stages of PRC decomposition can be interpreted in terms of the hypothesis stating that there are two hydrogen trioxide forms, stable and unstable ones, depending on their location in the condensate structure. The first stage of decomposition corresponds to degradation of H_2O_4, this process being accompanied by phase transformations in the solid condensate. Therefore, the apparent activation energy is high and substantially variable depending on the condensate composition. The next stage is decomposition of the unstable H_2O_3 in the solid crystallized condensate. The temperature ranges of the stages may partially overlap. The final stage corresponds to decomposition of stable H_2O_3 in the molten condensate. The fact that the last two stages involve decomposition of the same compound is confirmed by the similarity of the activation energies of these stages.

Studies of PRC by diffraction methods provided information on the phase composition of freshly prepared condensates and on its change on heating. The powder X-ray diffraction pattern of PRC formed from dissociated water vapour contains lines for ice and crystalline H_2O_2; also, a diffuse line is present at $\sim$3.46 Å, that is, between the amorphous H_2O_2 ($\sim$3.2 Å) and H_2O ($\sim$3.65 Å) lines. The same situation was found for the condensate formed upon an H_2O_2 discharge; in that case, the diffuse line was more intense. After 5 h at -115 to -110°C, complete crystallization of H_2O and H_2O_2 takes place in both cases. The diffuse line becomes weaker and completely disappears on heating to -78 °C. The X-ray diffraction patterns of the condensate obtained from hydrogen atoms and liquid ozone contain only a line for crystalline water and the diffuse line, which is much more intense than for other condensates. At -110 °C, the intensity of the ice line increases; and also the lines of crystalline H_2O_2 appear. This indicates that at -196 °C, the condensates contain components, other than H_2O or H_2O_2, that crystallize with difficulty and decompose at elevated temperatures (rather slowly at -110 °C) to give H_2O_2.[77] The PRC obtained by the reaction of hydrogen atoms with liquid ozone have also been studied by X-ray diffraction;[160] the results virtually coincided with those obtained by Tsentsiper *et al.*[77] No occluded oxygen was detected in the condensates.[160]

The electron diffraction data mainly support the results of X-ray diffraction.[77, 160] The electron diffraction patterns of the condensates prepared by the discharge in water vapour at -196 °C differ from those of simple condensates obtained from water vapour or $H_2O-H_2O_2$ vapour by the presence of a diffuse diffraction ring at 3.48 Å, that is, between the rings of amorphous water (3.69 Å) and amorphous $H_2O_2-H_2O$ solution (3.34 Å). At -120 °C, fast crystallization of H_2O and H_2O_2 takes place. The ring at 3.48 Å also disappears.[107, 161] The electron diffraction patterns of PRC obtained by the reaction of hydrogen atoms with liquid ozone also attest to the formation of new amorphous compounds.[162]

VII. Heats of decomposition of peroxy radical condensates

The decomposition of PRC is accompanied by considerable heat effects associated with the degradation of active components, hydrogen tri- and tetroxides. The first heating curves measured for PRC were reported by Hogg and Spice[108] and Bawn.[163] However, these curves are inapplicable for determining the reaction heats. Ghormley[155] roughly estimated the heat of the final stage of decomposition of molten PRC as 44 kcal (mol O_2)$^{-1}$.

The most detailed calorimetric and thermal studies of PRC were carried out by Nekrasov and co-workers[54, 74, 97, 98] and Levanov and co-workers.[164] According to Nekrasov and co-workers,[54, 74, 97, 98] decomposition of a PRC prepared from water vapour is accompanied by two exothermic and one endothermic effects. The first exotherm accompanies decomposition of the condensate in the solid phase in the range of 153–200 K, $\Delta_1H = -78 \pm 6$ (Refs 54, 97, 98) or -72 ± 9 (Refs 54, 74) kcal (mol O_2)$^{-1}$. It is clearly split in two, which is consistent with two gas evolution stages observed on heating of a solid condensate. Under these conditions, H_2O_4 and H_2O_3 decompose[37] and in the initial stage, the phase state of the PRC changes (crystallization).[77, 107, 161]

The endotherm, $\Delta H = +62$ cal (g H_2O_2)$^{-1}$ at 203–212 K (Refs 54, 74), $\Delta H = +50 \pm 5$ cal (condensate grams)$^{-1}$ at 203–218 K (Refs 54, 97, 98), corresponds to melting of the condensate.

The second exotherm accompanies decomposition of the molten condensate in the temperature range of 220–250 K: $\Delta_2H = -39 \pm 4$ (Refs 54, 97, 98), -34 ± 4 (Refs 54, 74) kcal (mol O_2)$^{-1}$. According to Levanov and co-workers,[164] this heat evolution occurs in the range of 240–265 K, Δ_2H is -31.2 ± 1.5 kcal (mol O_2)$^{-1}$. It has been shown[37] that the effect is caused by decomposition of only H_2O_3 rather than H_2O_4, as believed earlier.[54, 74, 97, 98] The reaction occurs in a liquid solution mainly composed of water and hydrogen peroxide and is not accompanied by any other processes involving heat evolution or absorption (except for the heat exchange with the environment).

Decomposition of the PRC obtained by the reaction $H + O_3$(liq) is accompanied by three exothermic and two endothermic effects. The first two exotherms correspond to solid-phase decomposition. Numerical values for these heats were not determined, since the kinetics of oxygen evolution was unknown; however, an approximate estimate of the heat evolved upon decomposition of the molten condensate, Δ_2H, was reported to be -36 kcal (mol O_2)$^{-1}$ (Refs 54, 74).

Martinez *et al.*[165] measured the heats of decomposition of PRC synthesized by the reaction $H + O_3$(liq) using a low-temperature isothermal calorimeter. The authors found again two key stages of condensate decomposition with oxygen evolution: $\Delta_1H = -71 \pm 12$ and $\Delta_2H = -44 \pm 10$ kcal (mol O_2)$^{-1}$.

The integral heat evolution of water vapour- and $H + O_3$(liq)-based condensates during heating from 77 to 273 K was measured by Csejka *et al.*[70] The H_2 $O_2 + H_2O$ mixtures with compositions similar to those of the liquid products formed upon PRC decomposition were used as reference materials. The presented overall heats [-17.8 ± 2.2 and -26.8 ± 2.6 kcal (mol O_2)$^{-1}$ for the PRCs obtained from water vapour and from $H + O_3$(liq), respectively] are at variance with the data cited above.[54, 74, 97, 98, 165] This is attributable to the superposition and partial counterbalancing of the heats of exo- and endothermic processes in determination of the integral heat of decomposition.

An important issue related to PRC decomposition heats is to determine the thermochemical properties of hydrogen

tetra- and trioxide on the basis of the heat data. The decomposition heats of the solid condensate are virtually inapplicable for this purpose,[37] because the crystal structure changes and phase transitions take place; therefore, it is impossible to distinguish between the contributions of particular processes to the total heat evolution. Meanwhile, in the final stage of decomposition of the molten condensate, degradation of H_2O_3 in the liquid phase

$$H_2O_3(aq) \longrightarrow H_2O(liq) + O_2(g) \quad (32)$$

is the only chemical reaction and is not accompanied by any other reactions. Hence, it is possible to estimate the thermochemical properties of hydrogen trioxide in the low-temperature solution.

It can be demonstrated [37, 164] that in the temperature range of 240 – 265 K, the enthalpy of formation of H_2O_3 in solution, $\Delta_f H(H_2O_3)(aq)$, is related to the enthalpy of decomposition reaction in the following way

$$\Delta_f H(H_2O_3)(aq) = -\Delta_2 H - 68.7 \pm 0.1 \text{ kcal mol}^{-1} \quad (33)$$

From this, one can easily derive an estimate for the enthalpy of formation of hydrogen trioxide in an aqueous solution based on experimental data (Table 5).

Table 5. Enthalpies of decomposition and formation of hydrogen trioxide in a low-temperature aqueous solution /kcal mol^{-1}.

T/K	$\Delta_{dec}H$	$\Delta_f H(H_2O_3)_{aq}$	Ref.
	Experimental data		
218 – 232	-39 ± 4	-30 ± 4.3	54, 97, 98
218 – 251	-34 ± 4	-35 ± 4.3	54, 74
240 – 265	-31.2 ± 1.5	-37.5 ± 1.6	164
	Calculated data [a]		
240 – 265		-36.8 ± 2.9	37

[a] The presented values taken from Ref. 37 are based on the data calculated in other works.[5, 23, 24, 27, 166 – 169]

Quite a number of publications [5, 23, 24, 27, 90, 166 – 169] present quantum chemical calculations of the enthalpy of formation of hydrogen trioxide in the gas phase at 298 K, the theoretical $\Delta_f H_{298}(H_2O_3)(g)$ value being -22.0 ± 1.0 kcal mol^{-1}. The enthalpies of formation in aqueous solution at 240 – 265 K and in the gas phase at 298 K are related by the expression [37, 164]

$$\Delta_f H_{240-265}(H_2O_3)(aq) = \quad (34)$$

$$= \Delta_f H_{298}(H_2O_3)(g) + \Delta_{hydr}H(H_2O_3) + 0.3 \text{ kcal mol}^{-1}$$

which can be used to compare the theoretical and experimental results. The estimated enthalpy of hydration, $\Delta_{hydr}H(H_2O_3)$, was -15.0 ± 1.9 kcal mol^{-1} and it did not depend on the temperature in the 200 – 273 K temperature range.[37] The experimental and theoretical enthalpies of formation of hydrogen trioxide in a low-temperature liquid solution are summarized in Table 5. It can be seen that the data from different sources are in satisfactory agreement with one another.

VIII. Conclusion

This review integrates and systematizes the available data on the synthesis and properties of peroxy radical condensates and studies of their active components — hydrogen tri- and tetroxides. The PRC synthesis provides a unique method for the preparation of hydrogen polyoxides for further investigation. Lately, a considerable progress has been made in hydrogen trioxide synthesis *via* reactions of ozone with particular organic compounds; this is the method of choice for H_2O_3 preparation. The synthesis of PRC is the only way to obtain specimens containing relatively high concentrations of hydrogen tetroxide. As shown in the review, effective methods for PRC synthesis have already been developed to date, the PRC composition and structure have been largely established, their decomposition kinetics and heats have been investigated and the mechanism of formation and kinetics of decomposition of hydrogen polyoxides as PRC components have been elucidated. The vibrational spectrum and the structure of hydrogen trioxide molecule were characterized in detail on the basis of its studies as a PRC component and also by other methods. By examination of the vibrational spectra of PRC, the existence of hydrogen tetroxide was proved and the vibrational spectrum of its oxygen skeleton was described. It is pertinent to determine the heats and kinetics of condensate decomposition by means of modern highly sensitive instrumental methods that can provide new information about the condensate structure and the properties of their active components. A more detailed experimental characterization of hydrogen tetroxide can be derived from examination of vibrational spectra of H_2O_4 in solid inert gas matrices at a relatively high dilution. Preparation of H_2O_4 in these matrices has not yet been accomplished; presumably, it could be done by low-temperature condensation of electrically dissociated gaseous $H_2 + O_2 +$ inert gas mixtures.

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