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BRIEF COMMUNICATIONS

Synthesis and Properties of Tetraalkylammonium Chlorides Peroxosolvates $(CH_3)_4NCl{\cdot}H_2O_2$ and $(C_2H_5)_4NCl{\cdot}H_2O_2$

K. V. Titova, V. P. Nikol'skaya, V. V. Buyanov,
O. B. Pudova, G. P. Karzhavina, and O. A. Zharkova

Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Russia
Federal State Unitary Enterprise "State Research Institute of Biological Instrument Engineering", Moscow, Russia

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Abstract—Tetraalkylammonium chlorides peroxosolvates $(CH_3)_4NCl{\cdot}H_2O_2$ and $(C_2H_5)_4NCl{\cdot}H_2O_2$ were synthesized. The composition of the solvates was proved by chemical analysis; their X-ray patterns, IR spectra, and thermograms were obtained. The solubility of the solvates in water and their stability in aqueous solutions were investigated.

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At present a reasonable number of peroxosolvates are known. They represent chemical compounds solvated by hydrogen peroxide: carbonates, phosphates, oxalates, and perchlorates [1]. Reactions of hydrogen peroxide with halides of alkali metals have been studied in detail. It was found that among the fluorides only lithium and sodium fluorides do not form peroxosolvates. The composition of peroxosolvates formed by potassium, rubidium, cesium, and ammonium depends on a mole ratio of a salt and hydrogen peroxide. Potassium fluoride crystallizes as the mono-, di-, and trisolvates $KF{\cdot}H_2O_2$, $KF{\cdot}2H_2O_2$, and $KF_3{\cdot}H_2O_2$; rubidium and cesium fluorides form peroxosolvates with an equal number of hydrogen peroxide molecules: $RbF{\cdot}1.5H_2O_2$ and $CsF{\cdot}1.5H_2O_2$; ammonium fluoride is solvated by one H_2O_2 mole [2, 3]. No information on the formation of alkali metal peroxosolvates was found in the literature accessible to the authors.

In the presented work the tetraalkylammonium chlorides peroxosolvates $(CH_3)_4NCl{\cdot}H_2O_2$ and $(C_2H_5)_4NCl{\cdot}H_2O_2$ were synthesized for the first time. The synthesis and study of this group of peroxosolvates expand knowledge of the hydrogen peroxide chemistry useful for the creation of its solid forms and for their further applications in disinfectology and other fields of decontamination.

EXPERIMENTAL

In this work hydrogen peroxide of concentration 45–50 wt % was used to synthesize tetramethyl- and tetraethylammonium peroxosolvates.

A 20 wt % solution of the hydroxide $(CH_3)_4NOH$ served as the mother substance for obtaining $(CH_3)_4NCl{\cdot}H_2O_2$. Tetramethylammonium hydroxide was transformed to tetramethylammonium chloride under the action of hydrochloric acid. The resulting solution was concentrated by an air flow (50–60°C) up to a viscous mass state. Then a hydrogen peroxide solution was added in an amount corresponding to the molar ratio $H_2O_2 : (CH_3)_4NCl = 5 : 1$; water and excess of hydrogen peroxide were removed by the same air flow.

Tetraethylammonium chloride peroxosolvate was prepared using solid chloride $(C_2H_5)_4NCl$ and hydrogen peroxide at the mole ratio $H_2O_2 : (C_2H_5)_4NCl = 5 : 1$. Water and H_2O_2 excess were removed in the same manner as in the synthesis of the tetramethylammonium salt.

Tetramethylammonium chloride peroxosolvate $(CH_3)_4NCl{\cdot}H_2O_2$ represents a nonhygroscopic colorless substance. In air at 20°C the peroxosolvate can be stored without losses of hydrogen peroxide for more than 10 days. Tetraethylammonium chloride peroxosolvate $(C_2H_5)_4NCl{\cdot}H_2O_2$ is hygroscopic.

The synthesized peroxosolvates were analyzed for the hydrogen peroxide content by the permanganatometric titration. Contents of hydrogen, carbon, and nitrogen were determined on a VARIO MIKRO cube analyzer. Chlorine contents were found by argentometry after determination of the H_2O_2 content by the permanganatometric titration. $(CH_3)_4NCl\cdot H_2O_2$. Found (%): C 32.94, Cl 32.30, N 9.50; H_2O_2 23.60, H_{total}(without H_2O_2) 10.20. $C_4H_{14}NClO_2$. Calculated (%): C 33.45, Cl 32.43, N 9.76; H_2O_2 23.70. H_{total}(without H_2O_2) 9.76. $(C_2H_5)_4NCl\ H_2O_2$. Found (%): C 47.27, Cl 17.7, N 7.00; H_2O_2 16.95, H_{total}(without H_2O_2) 10.3. $C_8H_{22}NClO_2$. Calculated (%): C 48.12, Cl 17.70, N 7.00; H_2O_2 17.00, H_{total}(without H_2O_2) 10.00.

The X-ray patterns were recorded by the powder technique on an ADP-2-01 diffractometer ($Cu_{K\alpha}$ radiation, Ni filter) using the program developed for "DRON" X-ray diffractometers for automation of the processes of the obtaining, treatment, and analyzing of data. The IR spectra of the synthesized solvates were recorded on a UR-20 spectrophotometer over the range of 400–4000 cm^{-1}. Samples were prepared in the form of suspensions in liquid paraffin. Thermograms were recorded on a 1500D derivatograph with a Pt-Pt/Rh thermoelectric couple, Al_2O_3 standard at the heating rate of 5 deg min^{-1}.

Table 1 contains the IR spectra of the synthesized compounds and, for comparison, the IR spectrum of potassium fluoride peroxosolvate, which in essence is the spectrum of bound hydrogen peroxide. Coincidence or proximity of bands of these spectra confirms the solvation of tetraalkylammonium chlorides under study by hydrogen peroxide.

Tetramethylammonium chloride peroxosolvate does not lose weight and keeps H_2O_2 content close to initial on continuous heating up to 125°C. Decomposition of the solvate begins at about 130°C and is accompanied by an appreciable endothermic effect. After 170°C the weight loss comes to the end. The tetraethylammonium solvate is also decomposed with an endothermic effect, but, unlike the tetramethylammonium solvate, in two stages. The first stage takes place at 125–175°C, then from 175 up to 225°C the disintegration process of the solvate stops, and the final disintegration occurs in the range of 225–250°C.

Tetramethylammonium chloride peroxosolvate is readily soluble in water, which is important in view of its possible practical application. The saturated solution of the solvate at 20°C contains 10.6% of H_2O_2, which corresponds to 44.7% of $(CH_3)_4NCl\cdot H_2O_2$. The solution is rather stable: for 25 days (Table 2) it loses one fourth part of hydrogen peroxide.

Solubility of tetraethylammonium chloride peroxosolvate in water is of the same order as that of tetraethylammonium. The saturated solution of $(C_2H_5)_4NCl\cdot H_2O_2$ contains 16.44% of H_2O_2, which corresponds to 83.6% of the solvate. In the initial stage of storage the solution is more stable than the solution of the tetramethylammonium peroxosolvate. The enhanced stability of the tetraethylammonium peroxosolvate solution is also retained in the late storage stages.

Obviously the synthesized peroxosolvates shall dissociate in aqueous solutions in two stages. The first stage will follow the equation

$$(CH3)_4NCl\cdot H_2O_2 \leftrightarrow (CH_3)_4N^+ + [Cl\cdot H_2O_2]^-,$$

and the second stage, the equation

$$[Cl\cdot H_2O_2]^- \leftrightarrow Cl^- + H_2O_2.$$

The cation $(CH_3)_4N^+$ will not undergo any transformations. The anion $[Cl\cdot H_2O_2]^-$ will be able to exhibit

Table 1. Absorption bands (cm^{-1}) of O–O and O–O–H groups in synthesized peroxosolvates and in $KF\cdot H_2O_2$

$(CH_3)_4NCl\cdot H_2O_2$	$(C_2H_5)_4NCl\cdot H_2O_2$	$KF\cdot H_2O_2$
960 s, stretching O–O	900 s, stretching O–O	885 s, stretching O–O
735 s, torsion	730 s, torsion	960 s, torsion
1410 s, bending O–O–H	1410 s, bending O–O–H	1485 s, bending O–O–H
1475 с, деформ. О–О–Н	1470 с, деформ. О–О–Н	1670 ср, деформ. О–О–Н
2790 s, stretching O–H	2790 s, stretching O–H	2600–2800 s.br, stretching O–H
3000–3400 s, unsymmetric stretching O–H	3200 s, unsymmetric stretching O–H	3000–3200 s, unsymmetric stretching O–H

Table 2. Stability of $(CH_3)_4NCl \cdot H_2O_2$ and $(C_2H_5)_4NCl \cdot H_2O_2$ in saturated aqueous solutions (20°C)

Parameter	Time, day									
	0	1	3	6	10	15	20	22	25	29
$(CH_3)_4NCl \cdot H_2O_2$										
H_2O_2 content, %	10.44	–	10.41	9. 62	9.43	8.40	8.04	–	7. 79	7. 30
H_2O_2 loses, %	0	–	0.3	7.9	9.7	19.5	23.0	–	25.4	27.00
$(C_2H_5)_4NCl \cdot H_2O_2$										
H_2O_2 content, %	5.78	6.16	6.26	5.87	5.80	5.36	–	5.30	–	5.05
H_2O_2 loses, %	0	0	0	0	0	7.3	–	8.4	–	12.7

enhanced decontamination activity due to a distortion on combining Cl^- and H_2O_2. Furthermore, as a result of its dissociation, a solution containing Cl^- ions and H_2O_2 molecules is formed. Such solutions are considered to exhibit a more effective toxicological antimicrobial action, which is connected with the influence of chloride ions on plasmochemical membranes and with the activation of solutions of mediators.

CONCLUSION

Tetramethyl- and tetraethylammonium chlorides peroxosolvates of the compositions $(CH_3)_4NCl \cdot H_2O_2$ and $(C_2H_5)_4NCl \cdot H_2O_2$ were synthesized. Their shelf stability in air and in solution and their thermal stability were studied. The synthesized compounds can be of interest for application in decontamination processes.

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