NMR study of the complex formation between tert-*butyl hydroperoxide and tetraalkylammonium bromides*

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Abstract The interaction between *tert*-butyl hydroperoxide and tetraalkylammonium bromides was studied by NMR spectroscopy in acetonitrile-d_3 at 298 K. The complex formation between the hydroperoxide molecule and corresponding quaternary ammonium salt was experimentally proven. The equilibrium constants of complex formation were determined by both ^{1}H and ^{13}C NMR spectroscopy. Complex stability decreases with increasing intrinsic volume of the tetraalkylammonium cation.

Keywords Hydroperoxide · Quaternary ammonium salts · NMR spectroscopy · Complex · Stability constant

Introduction

The investigation of supramolecular catalysis of organic peroxide decomposition is the current direction in the development of peroxide initiator chemistry. There is a wide range of catalytic systems for the radical decomposition of hydroperoxides [1, 2]. Quaternary ammonium salts occupy an important place among them. They are known to be effective catalysts of hydrocarbon radical oxidation [3]. Quantitative data on hydroperoxide decomposition in the presence of quaternary ammonium salts are necessary to

create a theoretical basis for controlling the reactivity of peroxide compounds in radical decomposition reactions.

The key feature of supramolecular hydroperoxide decomposition in the presence of tetraalkylammonium bromides (Alk_4NBr) is complex formation between the reactants [4]. Systematic kinetic investigations on the interaction between hydroperoxides and Alk_4NBr as well as the results of modeling allow the proposal of a structural model of the hydroperoxide-catalyst complex [4]. The structure of the complicated systems on the nanoscale [5, 6] as well as supramolecular [7–9] level can be accurately studied using modern instrumental methods. NMR spectroscopy is a major experimental tool of modern chemistry and widely used to study the structure and reactivity of supramolecular systems [10, 11].

The purpose of this work was to experimentally prove the complex formation in the reaction of the *tert*-butyl hydroperoxide interaction with tetraalkylammonium bromides by NMR ^{1}H and ^{13}C spectroscopy.

Results and discussion

The effect of Alk_4NBr on the signal position of $(CH_3)_3C-O-OH$ in the proton magnetic resonance spectrum was investigated to confirm the complex formation between *tert*-butyl hydroperoxide and tetraalkylammonium bromides. There is no $(CH_3)_3C-O-OH$ decomposition in experimental conditions (reaction rate constant of the hydroperoxide thermolysis in acetonitrile is k_{term}^{298} = 1.47 × 10^{-10} s^{-1} [12]). A signal at 1.18 ppm in the $(CH_3)_3C-O-OH$ ^{1}H NMR spectrum corresponds to protons in the methyl groups, and the chemical shift at 8.80 ppm is assigned to the hydroperoxide group ($-CO-OH$) proton (Fig. 1). Changing the hydroperoxide concentration

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within $(2.1–500.0) \times 10^{-3}$ mol dm^{-3} does not lead to a shift in the –CO–OH group proton signal in the spectrum. Addition of an equivalent amount of tetraalkylammonium bromide to the system leads to a shift in the –CO–OH group proton signal to the side of weak fields without splitting or significant broadening (Fig. 1).

Subsequent ^{1}H NMR spectroscopic studies were carried out in conditions of quaternary ammonium salt excess. The concentration of (CH$_3$)$_3$C–O–OH in all experiments was constant (0.03 mol dm^{-3}), while the concentration of Alk$_4$NBr varied within the range of 0.10–0.62 mol dm^{-3}. The monotonous shifting of the NMR signal with increasing of the Alk$_4$NBr concentration without splitting and significant broadening shows a fast exchange between the free and bonded forms of hydroperoxide. This character of the signal changing of the hydroperoxide group proton in the presence of Alk$_4$NBr indicates the formation of a complex between hydroperoxide and Alk$_4$NBr in the system. Thus, the observed chemical shift of the –CO–OH

group proton (δ) in the spectrum of the (CH$_3$)$_3$C–O–OH–Alk$_4$NBr mixture is an averaged signal of the free (δ_{ROOH}) and complexed (δ_{comp}) hydroperoxide molecule.

Nonlinear dependences of the changes in the proton chemical shift $\Delta\delta$

$(\Delta\delta = \delta - \delta_{ROOH})$ of the hydroperoxide group on the Alk$_4$NBr initial concentration (Fig. 2a) were obtained.

The Foster-Fyfe equation can be used [13] in conditions of Alk$_4$NBr excess and formation of the 1:1 complex for the analysis of the experimentally obtained dependence:

$$\Delta\delta/[\text{Alk}_4\text{NBr}] = -K_C\Delta\delta + K_C\Delta\delta_{max} \tag{1}$$

where K_C is the equilibrium constant of the complex formation between hydroperoxide and the corresponding Alk$_4$NBr, dm^3 mol^{-1}; $\Delta\delta_{max}$ is the difference between the chemical shift of the –CO–OH group proton of complexed and free hydroperoxide ($\Delta\delta_{max} = \delta_{comp} - \delta_{ROOH}$), ppm.

Dependences of the $\Delta\delta$ on the Alk$_4$NBr initial concentration are linear (Fig. 2b) in the coordinates of Eq. (1).
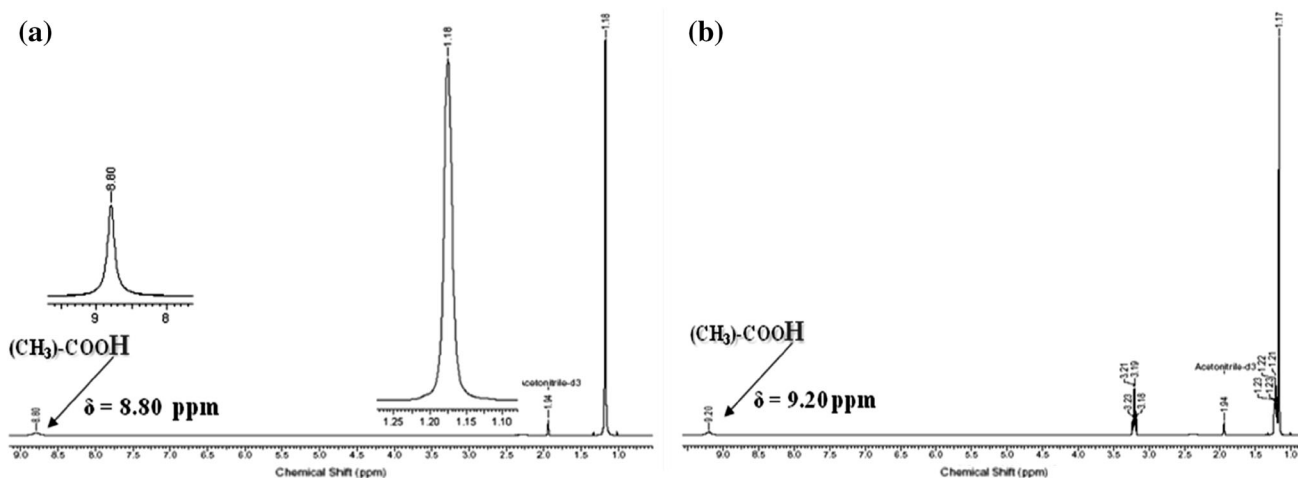

Fig. 1 ^{1}H NMR spectra of the (CH$_3$)$_3$C–O–OH (**a**) and (CH$_3$)$_3$C–O–OH in the presence of Et$_4$NBr (**b**) in CD$_3$CN, [ROOH]$_0$ = [Et$_4$NBr]$_0$ = 0.1 mol dm^{-3}, 298 K
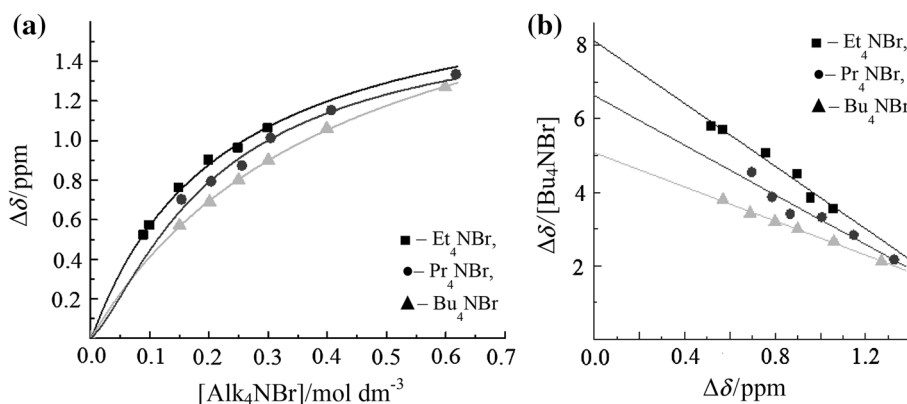

Fig. 2 Dependences of changes in the proton chemical shift of *tert*-butyl hydroperoxide on the initial Alk$_4$NBr concentration in the direct (**a**) and Foster-Fyfe equation (**b**) coordinates ([ROOH]$_0$ = 0.03 mol dm^{-3}, [Et$_4$NBr] = 0.09–0.30 mol dm^{-3}, [Pr$_4$NBr] = 0.15–0.60 mol dm^{-3}, [Bu$_4$NBr] = 0.15–0.60 mol dm^{-3}, 298 K, CD$_3$CN)

Table 1 The thermodynamic parameters of complex formation between $(CH_3)_3C-O-OH$ and Alk_4NBr

System	K_C/dm^3 mol^{-1}		δ_{comp}/ppm		$\Delta_{comp}^{298K}G$ /kJ mol^{-1}	
	^{1}H NMR	^{13}C NMR	^{1}H NMR	^{13}C NMR	^{1}H NMR	^{13}C NMR
ROOH + Et$_4$NBr	4.4 ± 0.4	4.6 ± 0.6	10.63 ± 0.08	26.6 ± 0.2	-3.64	-3.78
ROOH + Pr$_4$NBr	3.4 ± 0.4	3.5 ± 0.4	10.72 ± 0.09	26.6 ± 0.3	-3.02	-3.11
ROOH + Bu$_4$NBr	2.3 ± 0.1	2.4 ± 0.2	10.95 ± 0.03	26.9 ± 0.8	-2.09	-2.12

The equilibrium constants of the complex formation between hydroperoxide and Alk_4NBr (K_C) and the chemical shift of the $-CO-OH$ group proton of complexed hydroperoxide (δ_{comp}) were determined and are listed in Table 1.

The effect of the Alk_4NBr on *tert*-butyl hydroperoxide was investigated by ^{13}C NMR spectroscopy. There are two signals in the ^{13}C NMR spectra of *tert*-butyl hydroperoxide: the first one at 26.06 ppm corresponds to the methyl group carbon atoms and the second one at 80.44 ppm to the $-CO-OH$ moiety carbon. Addition of Alk_4NBr to the hydroperoxide solution leads to a shift of both signals. The methyl group's carbon atom signal is used for systematic study because of high intensity and short experiment time for each sample as compared with the signal of $-CO-OH$ moiety carbon.

The fact that the tetraalkylammonium bromides affect the signal of the methyl group carbon and do not affect the corresponding proton signal may indicate that the presence of salt varies slightly the distribution of electron density in $-CH_3$ groups of the hydroperoxide molecule, but change of the molecular conformation is possible. A similar effect is shown for the binging of tetraalkylammonium salts with *meso*-octamethylcalix [4] pyrrole [14].

The relative chemical shifts in ^{13}C NMR also provide a tool for obtaining the stabilization constant of the complex experimentally. ^{13}C NMR spectroscopic studies also were carried out in the same conditions as in the ^{1}H NMR ones. Increasing the Alk_4NBr concentration in the system leads to a shift of the $-CH_3$ group carbon signal to the side of the weak fields without splitting or significant broadening. This character of signal changing of the methyl group in the presence of Alk_4NBr (Fig. 3) indicates the formation of a complex between hydroperoxide and Alk_4NBr in the system.

These experimental dependences of the $\Delta\delta$ on the Alk_4NBr initial concentration are linear (Fig. 3) in the Foster-Fyfe equation coordinates. This enables determining the equilibrium constant of complexation (K_C) and the chemical shift of the $-CH_3$ group carbon atoms of complex bonded hydroperoxide (δ_{comp}). The corresponding values are listed in Table 1. These Kc values coincide with those determined by ^{1}H NMR spectroscopy.

It should be noted that there are no significant changes in the chemical shifts of the methyl and methylene groups' protons of Alk_4NBr in the spectra of $(CH_3)_3C-O-OH-Alk_4NBr$ solutions. However, the K_C value depends on the quaternary cation structure and limiting equivalent conductivity (λ_i^∞), namely it decreases with increasing of the intrinsic volume of the salt cation (V) and with λ_i^∞ decreasing (Fig. 4).

So, dependence of the K_C value on the structure of the quaternary ammonium cation indicates cation participation in the complex formation, which is consistent with a key role of the anion [3] and regulating action of the cation [15, 16] in hydroperoxide molecule activation. A similar effect has already been observed in CDCl$_3$ solution for the hydroperoxide—Alk_4NBr systems [20]. The equilibrium constant values also decrease with increasing intrinsic cation volume, and this dependence effect remains over the temperature range 297–313 K. $\Delta_{comp}H$ values of the complex formation are within -20 to -9 kJ mol^{-1} in CDCl$_3$ solution, which corresponds to a weak hydrogen bond. Thus, the cation effect is not due to the solvent-specific properties only, but is also caused by the complex structure.

One of the possible structure models of the complex under consideration is a substrate-separated ion pair. This model is characterized by the location of hydroperoxide in the space between the cation and anion of the onium salt. The solvent molecule is also taken into account (Fig. 5a). We can propose an alternative model for the complex, wherein the cation is not directly bonded with the hydroperoxide, but regulates the anion reactivity (Fig. 5b). In this case, the hydroperoxide molecule is attacked by the solvent-separated ion pair.

The semi-empirical AM1 calculations showed the structural reorganization of the $-COOH$ fragment geometry in the complex. This process requires energy; thus, the complex stability is not high. This is in accordance with the experimental facts. Such reorganization leads to peroxide bond activation and increasing of the hydroperoxide reactivity.

Further investigations to detail the structure and stability of the complex in the framework of DFT methods are required.

Thus, complex formation between *tert*-butyl hydroperoxide and Alk_4NBr has been demonstrated by ^{1}H and ^{13}C NMR spectroscopy. The thermodynamic characteristics of $(CH_3)_3C-O-OH-Alk_4NBr$ complex formation were determined. It is shown that the stability of these associates

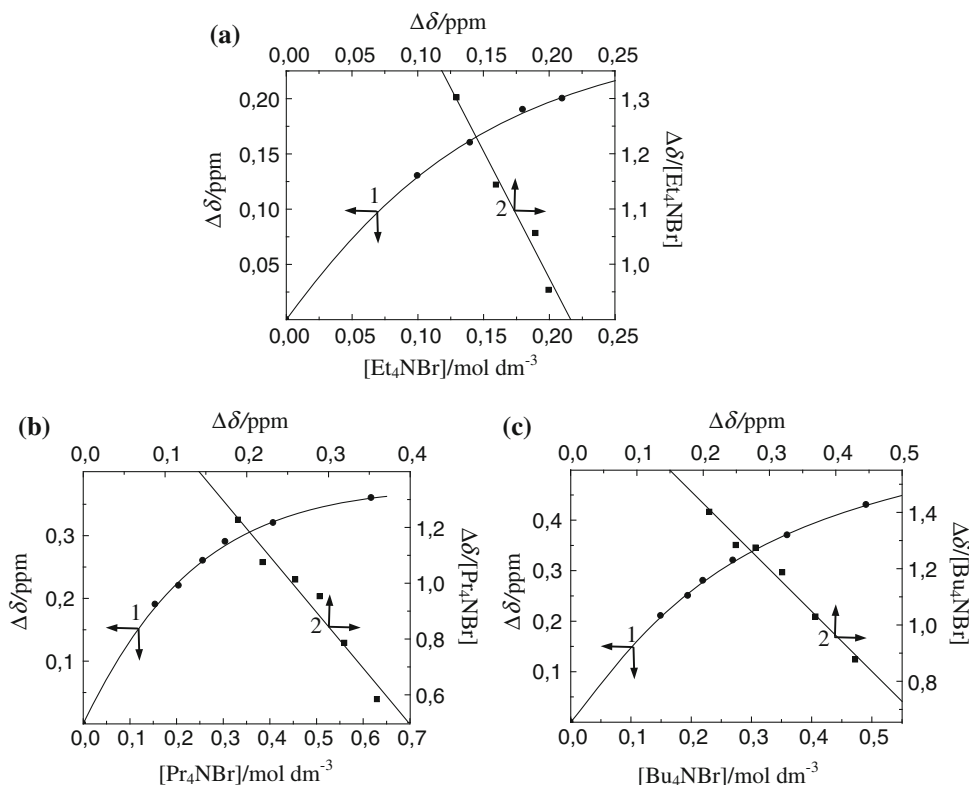**Fig. 3** Dependences of changes in the –CH$_3$ carbon atoms' chemical shift of *tert*-butyl hydroperoxide on the Et$_4$NBr (**a**), Pr$_4$NBr (**b**), and Bu$_4$NBr (**c**) the initial concentration in direct (1) and Foster-Fyfe equation (2) coordinates ([ROOH]$_0$ = 0.03 mol dm^{-3}, [Et$_4$NBr] = 0.10–0.21 mol dm^{-3}, [Pr$_4$NBr] = 0.15–0.62 mol dm^{-3}, [Bu$_4$NBr] = 0.15–0.49 mol dm^{-3}, 298 K, CD$_3$CN)
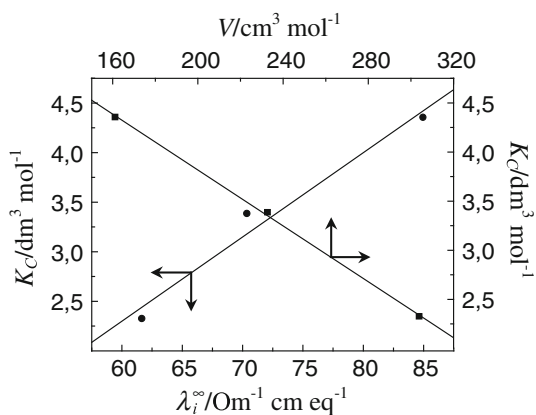

Fig. 4 Dependences of the equilibrium constant of the complex formation K_C from the intrinsic cation volume V of the Alk$_4$NBr and λ_i^∞. Values of V and λ_i^∞ are taken from [18, 19], respectively

decreases with increasing intrinsic volume of the salt cation (V) and with $\Delta_{comp}H$ decreasing.

Experimental

^{1}H and ^{13}C NMR spectroscopy investigations of the hydroperoxide and hydroperoxide-Alk$_4$NBr solutions were carried out in CD$_3$CN at 298 K. The NMR spectra were recorded on a Bruker Avance 400 using tetramethylsilan (TMS) as an internal standard.

Tert-butyl hydroperoxide (C$_4$H$_{10}$O$_2$) was purified according to [17]; its purity (99.8 %) was controlled by the iodometry method. ^{1}H NMR (400 MHz, CD$_3$CN): δ = 1.18 (s, 9H, –CH$_3$), 8.80 (s, 1H, –COOH) ppm; ^{13}C NMR (100 MHz, CD$_3$CN): δ = 26.06 (–CH$_3$), 80.44 (–COOH) ppm. Active oxygen (mass %): calculated 17.7, found 17.3.

Tetraalkylammonium bromides (Et$_4$NBr, Pr$_4$NBr, Bu$_4$NBr) were Fluka reagents and twice recrystallized from acetonitrile solution by the addition of diethyl ether excess. The salt purity was controlled by argentummetric titration with potentiometric fixation of the equivalent point. Tetraalkylammonium bromides (Alk$_4$NBr) were stored in a box dried with P$_2$O$_5$.

Tetraethylammonium bromide (C$_8$H$_{20}$BrN): m.p.: 285 °C (dec.); ^{1}H NMR (400 MHz, CD$_3$CN): δ = 1.20 (t, J = 8.0 Hz, 12H, –CH$_2$–*CH$_3$*), 3.20 (q, J = 8.0 Hz, 8H, –*CH$_2$*–CH$_3$) ppm; ^{13}C NMR (100 MHz, CD$_3$CN): δ = 7.75 (–CH$_2$–*CH$_3$*), 53.05 (–*CH$_2$*–CH$_3$) ppm.

Tetrapropylammonium bromide (C$_{12}$H$_{28}$BrN): m.p.: 270 °C (dec.); ^{1}H NMR (400 MHz, CD$_3$CN): δ = 0.93 (t,

Fig. 5 3D structural models of the *tert*-butyl hydroperoxide—Et$_4$NBr complex
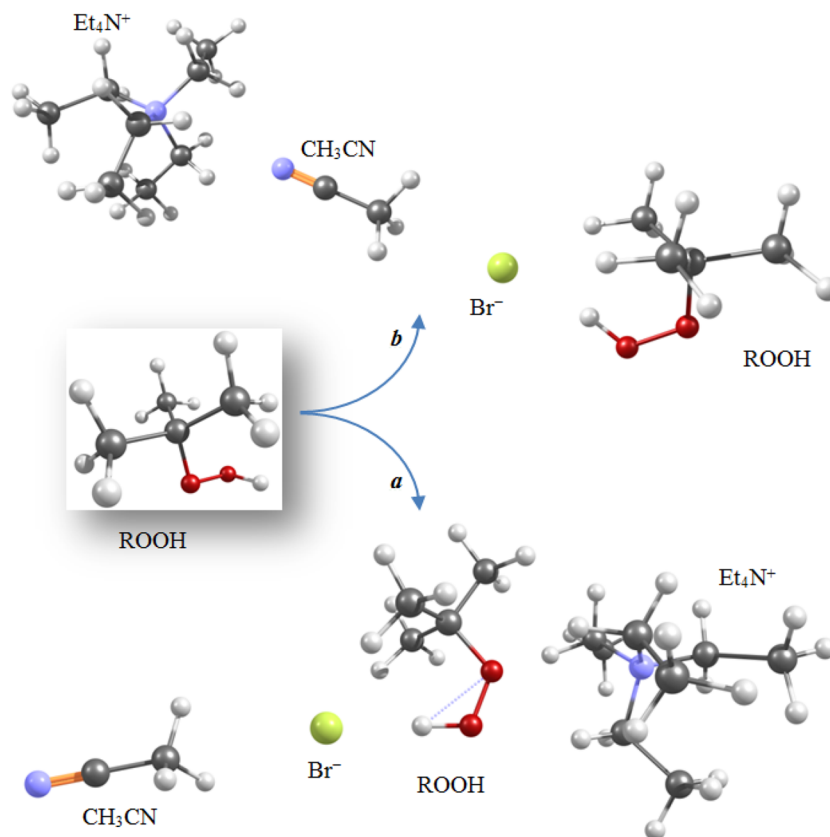
$J = 8.0$ Hz, 12H, –CH$_2$–CH$_2$–*CH$_3$*), 1.64 (s, $J = 8.0$ Hz, 8H, –CH$_2$–*CH$_2$*–CH$_3$), 3.08 (t, $J = 8.0$ Hz, 8H, –*CH$_2$*–CH$_2$–CH$_3$) ppm; ^{13}C NMR (100 MHz, CD$_3$CN): $\delta = 10.78$ (–CH$_2$–CH$_2$–*CH$_3$*), 16.05 (–CH$_2$–*CH$_2$*–CH$_3$), 61.01 (–*CH$_2$*–CH$_2$–CH$_3$) ppm.

Tetrabutylammonium bromide (C$_{16}$H$_{32}$BrN): m.p.: 103–104 °C; ^{1}H NMR (400 MHz, CD$_3$CN): $\delta = 0.97$ (t, $J = 8.0$ Hz, 12H, –CH$_2$–CH$_2$–CH$_2$–*CH$_3$*), 1.35 (s, $J = 8.0$ Hz, 8H, –CH$_2$–CH$_2$–*CH$_2$*–CH$_3$), 1.60 (qv, $J = 8.0$ Hz, 8H, –CH$_2$–*CH$_2$*–CH$_2$–CH$_3$), 3.08 (t, $J = 8.0$ Hz, 8H, –*CH$_2$*–CH$_2$–CH$_2$–CH$_3$) ppm; ^{13}C NMR (100 MHz, CD$_3$CN): $\delta = 13.67$ (–CH$_2$–CH$_2$–CH$_2$–*CH$_3$*), 20.24 (–CH$_2$–CH$_2$–*CH$_2$*–CH$_3$), 24.21 (–CH$_2$–*CH$_2$*–CH$_2$–CH$_3$), 59.28 (–*CH$_2$*–CH$_2$–CH$_2$–CH$_3$) ppm.

Quantum chemical calculations of the equilibrium structures of the hydroperoxide molecule as well as tetraethylammonium bromide and (CH$_3$)$_3$C–O–OH–Et$_4$NBr complexes were carried out by AM1 semi-empirical method implemented in MOPAC2012^{TM} package [21]. The RHF method was applied to the calculation of the wave function. Optimization of hydroperoxide structure parameters was carried out by eigenvector following procedure. The molecular geometry parameters were calculated with boundary gradient norm 0.01. The nature of the stationary points obtained was verified by calculating the vibrational frequencies at the same level of theory.

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