

¹H NMR STUDY OF THE TERT-BUTYL HYDROPEROXIDE INTERACTION WITH TETRAALKYL AMMONIUM BROMIDES

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ABSTRACT

The interaction between the tert-butyl hydroperoxide and tetraalkylammonium bromides (Et₄NBr, Pr₄NBr, Bu₄NBr) have been studied by ¹H NMR spectroscopy in chloroform-d at 297 - 313 K. The complex formation between the hydroperoxide molecule and quaternary ammonium salt has been experimentally proved. The equilibrium constants of complex formation (K_C) as well as complexation enthalpy and entropy have been determined. The tert-butyl hydroperoxide forms a complex with Et₄NBr, Pr₄NBr, and Bu₄NBr with the complex formation enthalpy: (- 19.5 ± 1.3), (- 16.6 ± 2.7), (- 8.8 ± 2.1) kJ·mol⁻¹ respectively.

Keywords: tert-butyl hydroperoxide, tetraalkylammonium bromides, ¹H NMR spectroscopy, complexation, thermodynamic parameters

INTRODUCTION

The role of the salt cation in the complex formation is discussed. Investigation of the mechanisms of the peroxide compounds supramolecular reactions is of great importance for molecular biology, medicine, cosmetics and food industry, petroleum chemistry and catalysis. The decisive role in the investigation of objects of this field belongs to the development of modern physical methods of studying the structure and properties, including NMR

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spectroscopy, which allows exploring even relatively labile supramolecular assemblies that are characterized by low-energy non-covalent interactions [1].

The results presented in this paper are related to the fundamental problem of molecular recognition in the reactions of the hydroperoxides with onium salts. Quaternary ammonium salts exhibit catalytic action in the reactions of the hydroperoxides radical decomposition [2, 3]. It results in the proceeding of liquid-phase oxidation process of hydrocarbons with molecular oxygen under mild conditions [4]. The results of the kinetic studies have shown that the catalysis of the hydroperoxide decomposition by onium salts includes the step of the complex formation [2, 3].

The present work deals with the study of the interaction between tert-butyl hydroperoxide and tetraalkylammonium bromides (Alk_4NBr) by ^1H NMR spectroscopy and determination of the thermodynamic parameters of the complex formation between them.

EXPERIMENTAL

Tert-butyl hydroperoxide ($(\text{CH}_3)_3\text{C-O-OH}$) was purified according to [5], its purity (99.8 %) was controlled by iodometry method. Tetraalkylammonium bromides (Et_4NBr , Pr_4NBr , Bu_4NBr) were twice recrystallized from acetonitrile solution by addition of diethyl ether excess. The salts purity (99.6%) was determined by argentometric titration with potentiometric fixation of the equivalent point. Tetraalkylammonium bromides (Alk_4NBr) were stored in box dried with P_2O_5 .

^1H NMR spectroscopy investigations of the hydroperoxide and hydroperoxide – Alk_4NBr solutions were carried out in CDCl_3 at 297-313 K. The ^1H NMR spectra were recorded on a Bruker Avance 400 (400 MHz) using tetramethylsilan (TMS) as an internal standard.

Tert-butyl hydroperoxide ($(\text{CH}_3)_3\text{C-O-OH}$) ^1H NMR (400 MHz, CDCl_3 , 297 K): $\delta = 1.27$ (s, 6 H, $-\text{CH}_3$), 7.24 (s, 1 H, $-\text{COOH}$) ppm. Active oxygen (mas %): calculated – 17.7, found – 17.3.

Tetraethylammonium bromide (Et_4NBr) m.p._{decomp} = 285°C, ^1H NMR (400 MHz, CDCl_3 , 297 K): $\delta = 1.41$ (t, $J = 8.0$ Hz, 12 H, $-\text{CH}_3$), 3.50 (q, $J = 8.0$ Hz, 8 H, $-\text{CH}_2-$) ppm.

Tetrapropylammonium bromide (Pr_4NBr) m.p._{decomp} = 270°C, ^1H NMR (400 MHz, CDCl_3 , 297 K): $\delta = 1.07$ (t, $J = 8.0$ Hz, 12 H, $-\text{CH}_3$), 1.79 (sec, $J = 8.0$ Hz, 8 H, $-\text{CH}_2-$), 3.37 (t, $J = 8.0$ Hz, 8 H, $-\text{CH}_2-$) ppm.

Tetrabutylammonium bromide (Bu_4NBr) m.p. = 103-104°C, ^1H NMR (400 MHz, CDCl_3 , 297 K): $\delta = 1.01$ (t, $J = 8.0$ Hz, 12 H, $-\text{CH}_3$), 1.47 (sec, $J = 8.0$ Hz, 8 H, $-\text{CH}_2-$), 1.71 (qv, $J = 8.0$ Hz, 8 H, $-\text{CH}_2-$), 3.40 (t, $J = 8.0$ Hz, 8 H, $-\text{CH}_2-$) ppm.

RESULTS AND DISCUSSION

Systematic studies of the kinetics of hydroperoxides [3, 4], cyclohexanone peroxides [4], diacyl peroxides [6] decomposition in the presence of quaternary ammonium salts have shown that the first reaction stage is the formation of complex intermediate between peroxide and catalyst. The structural model of the peroxide - onium salt reactive complexes was proposed based on the results of molecular modeling [3, 4]. The structural reorganization of the peroxide fragment containing the molecule reaction center ($-\text{O-O}-$ bond) is a key factor in

the chemical activation of peroxide compounds in the presence of quaternary ammonium salts. This decreases the strength of the peroxide bond. The structural feature of the hydroperoxide - Alk₄NBr complexes is the configuration of the peroxide moiety, which is similar to the peroxide configuration in the reaction transition state. These facts indicate the supramolecular mechanism of peroxide activation in the presence of quaternary ammonium salts.

The spectroscopic methods are widely used for the identification and characterization of homo - and hetero association of hydroperoxide compounds [7, 8]. The interaction between tetraalkylammonium bromides and tert-butyl hydroperoxide can be observed by relative change of the chemical shifts in the NMR spectra. Thus the effect of Alk₄NBr on the signal position of hydroperoxide in the proton magnetic resonance spectrum has been investigated to confirm the complex formation between tert-butyl hydroperoxide and tetraalkylammonium bromides. There is no (CH₃)₃C-O-OH decomposition in experimental conditions. In the ¹H NMR spectrum of (CH₃)₃C-O-OH signal at 1.27 ppm corresponds to protons of the methyl groups, and chemical shift at 7.24 ppm is assigned to proton of the hydroperoxide group (-CO-OH). Changing of hydroperoxide concentration within (9.0 – 20.0)·10⁻³ mol dm⁻³ does not lead to a shift of the hydroperoxide group proton signal in spectrum. Addition of an equivalent amount of tetraalkylammonium bromide to the system leads to a shift -CO-OH group proton signal to the side of the weak fields without splitting or significant broadening (Figure 1).

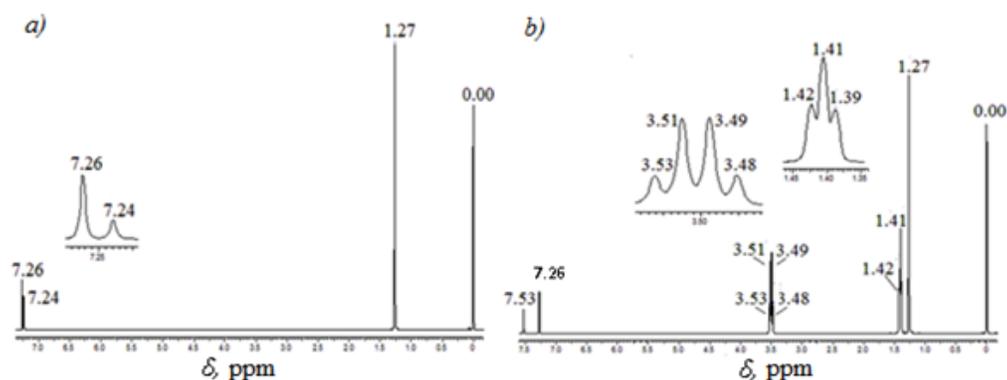


Figure 1. ¹H NMR spectra of the (CH₃)₃C-O-OH (a) and (CH₃)₃C-O-OH in the presence of Et₄NBr (b) in CDCl₃, [ROOH]₀ = [Et₄NBr]₀ = 0,02 mol·dm⁻³, 297 K.

Subsequent ¹H NMR spectroscopic studies were carried out in conditions of the quaternary ammonium salt excess. The concentration of (CH₃)₃C-O-OH in all experiments was constant (0.02 mol·dm⁻³), while the concentration of Alk₄NBr was varied within the range of 0.10 - 0.65 mol·dm⁻³. The monotonous shifting of the NMR signal with increasing of Alk₄NBr concentration without splitting and significant broadening shows fast exchange between the free and bonded forms of the hydroperoxide. Such character of signal changing of the hydroperoxide group proton in the presence of Alk₄NBr (Figure 2 - a) indicates the formation of a complex between hydroperoxide and Alk₄NBr in the system. Thus, observed chemical shift of the -CO-OH group proton (δ, ppm) in the spectrum of (CH₃)₃C-O-OH - Alk₄NBr mixture is averaged signal of the free (δ_{ROOH}, ppm) and complexed (δ_{comp}, ppm) hydroperoxide molecule. A nonlinear dependence of the changes of the proton chemical shift

$\Delta\delta$ ($\Delta\delta = \delta - \delta_{\text{ROOH}}$) of hydroperoxide group on the Alk_4NBr initial concentration (Figure 2 – a) was obtained. In conditions of Alk_4NBr excess and formation of the 1:1 complex for the analysis of the experimentally obtained dependence the Foster - Fyfe equation can be used [1]:

$$\Delta\delta[\text{Alk}_4\text{NBr}] = -K_C\Delta\delta + K_C\Delta\delta_{\text{max}}, \quad (1)$$

where K_C – the equilibrium constant of the complex formation between hydroperoxide and Alk_4NBr , $\text{dm}^3 \cdot \text{mol}^{-1}$; $\Delta\delta_{\text{max}}$ – the difference between the chemical shift of the -CO-OH group proton of complexed and free hydroperoxide ($\Delta\delta_{\text{max}} = \delta_{\text{comp}} - \delta_{\text{ROOH}}$), ppm.

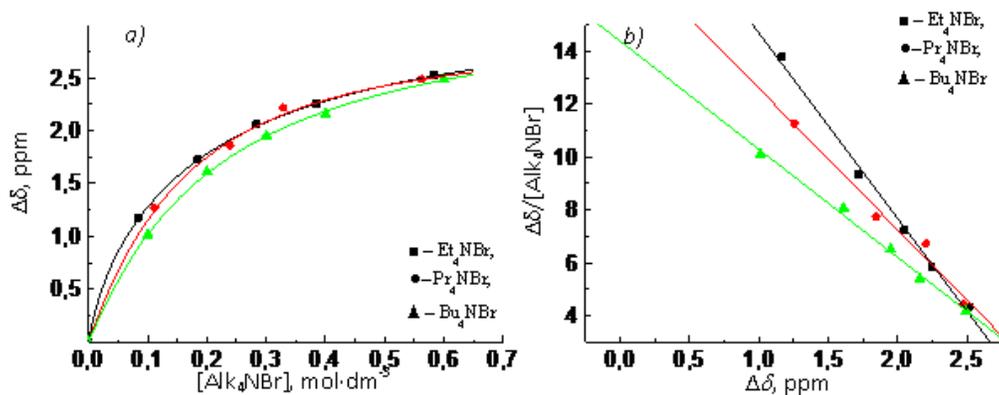


Figure 2. Dependence of change of the proton chemical shift of tert-butyl hydroperoxide on the Alk_4NBr initial concentration in direct (a) and Foster - Fyfe equation (b) coordinates ($[\text{ROOH}]_0 = 0,02 \text{ mol dm}^{-3}$, 297 K, CDCl_3)

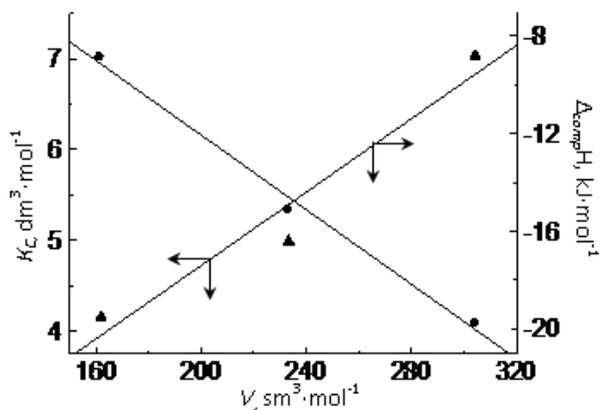


Figure 3. Dependence of the equilibrium constant of the complex formation K_c^{297} and enthalpy of the complexation $\Delta_{\text{comp}}H$ from the intrinsic cation volume V of the Alk_4NBr . Values of V are taken from [10].

This dependence of the $\Delta\delta$ on the Alk_4NBr initial concentration is linear (Figure 2 - b) in the coordinates of equation (1).

The equilibrium constants of the complex formation between hydroperoxide and Alk₄NBr (K_C) and the chemical shift of the -CO-OH group proton of complexed hydroperoxide were determined and listed in Table 1. The K_C value depends on the quaternary cation structure, namely it decreases with increasing of the intrinsic volume of the salt cation (V) (Figure 3). Chemical shift of the -CO-OH group proton of complexed hydroperoxide molecule (δ_{comp}) is slightly dependent on the temperature as well as on the cation size.

The temperature dependences of K_C value are linear in van't Hoff isotherm equation coordinates. The values of the enthalpy ($\Delta_{comp}H$) and entropy ($\Delta_{comp}S$) of the (CH₃)₃C-O-OH - Alk₄NBr complexation reaction were obtained and listed in Table 1.

Table 1. The thermodynamic parameters of complex formation between (CH₃)₃C-O-OH and Alk₄NBr

Alk ₄ NBr	T, K	K_C , dm ³ ·mol ⁻¹	δ_{comp}	$\Delta_{comp}H$, kJ mol ⁻¹	$\Delta_{comp}S$, J·mol ⁻¹ ·K ⁻¹	$\Delta_{comp}^{297}G$, kJ mol ⁻¹
Et ₄ NBr	297	7.02 ± 0.30	10.33 ± 0.08	-19.5 ± 1.3	-49.5 ± 4.4	-4.81
	303	6.08 ± 0.05	10.47 ± 0.02			
	308	5.46 ± 0.05	10.44 ± 0.02			
	313	4.65 ± 0.51	10.51 ± 0.23			
Pr ₄ NBr	297	5.34 ± 0.13	10.62 ± 0.20	-16.4 ± 2.7	-41.7 ± 8.9	-4.14
	303	4.62 ± 0.09	10.73 ± 0.02			
	308	3.96 ± 0.04	10.52 ± 0.04			
	313	3.87 ± 0.28	10.65 ± 0.14			
Bu ₄ NBr	297	4.09 ± 0.18	10.77 ± 0.08	-8.8 ± 2.1	-17.8 ± 6.8	-3.48
	303	4.05 ± 0.06	10.73 ± 0.03			
	308	3.64 ± 0.29	10.64 ± 0.14			
	313	3.45 ± 0.05	10.70 ± 0.03			

The values of the $\Delta_{comp}H$ for the hydroperoxide complex with investigated salts are negative and lie in the range from -9 to -20 kJ mol⁻¹, that corresponds to the formation of weak hydrogen bonds [11].

The values of the Gibbs free energy of complexation have low negative values. The strength of the H-bond in the complex decreases (Figure 3) with the intrinsic volume of the salt cation increasing.

It should be noted that there are no significant changes in the chemical shifts of methyl and methylene groups' protons of the Alk₄NBr in the spectra of ROOH - Alk₄NBr solutions. Consequently, the cation does not interact directly with hydroperoxide, unlike bromide anion that forms a hydrogen bond with the hydroperoxide group. However, dependence of the (CH₃)₃C-O-OH - Alk₄NBr complexes thermodynamic characteristics on the structure of quaternary ammonium cation obtained in this work indicates cation participation in the complex formation.

CONCLUSION

Thus, the formation of a complex between the tert-butyl hydroperoxide and Alk_4NBr has been demonstrated by ^1H NMR spectroscopy method. Thermodynamic parameters of complex formation have been determined. The strength of the H-bond in the complex decreases with increase in the intrinsic volume of the salt cation.

REFERENCES

- [1] Fielding, L. Determination of Association Constants (K_a) from Solution NMR Data *Tetrahedron*. 2000, 56, 6151-6170.
- [2] Turovskij, N. A.; Antonovskij, V. L.; Opeida, I. A.; Nikolaevskij, A. N.; Shuflet'uk, V. N. Vliyanie onievych solej na kinetiku raspada gidroperoxida kumila (Effect of the onium salts on the kinetics of cumene hydroperoxide decomposition) *Khimicheskaya Fizika*. 2001, 20, 41-45.
- [3] Turovskij, N. A.; Raksha, E. V.; Gevus, O. I.; Opeida, I. A.; Zaikov G. E. Activation of 1-Hydroxycyclohexyl Hydroperoxide decomposition in the presence of Alk_4NBr *Oxid. Commun.* 2009, 32, 69-77.
- [4] Turovskij, N. A.; Opeida, I. A.; Turovskaya, E. N.; Raksha, O. V.; Kuznetsova, N. O.; Zaikov, G. E. Kinetics of radical chain cumene oxidation initiated by α -oxycyclohexylperoxides in the presence of Et_4NBr *Oxid. Commun.* 2006, 29, 249-257.
- [5] Hock, H.; Lang, S. Autoxydation von Kohlenwasserstoffen, IX. Mitteil.: Über Peroxyde von Benzol-Derivaten (Autoxidation of hydrocarbons IX. Msgs. About peroxides of benzene derivatives) *Chem. Ber.* 1944, 77, 257-264.
- [6] Turovskij, N. A.; Pasternak, E. N.; Raksha, E. V.; Golubitskaya, N. A.; Opeida, I. A.; Zaikov G. E. Supramolecular reaction of lauroyl peroxide with tetraalkylammonium *Bromides Oxid. Commun.* 2010, 33, 485-501.
- [7] Syroezhko, A. M.; Proskuryakov, V. A. Complex formation of carbonyls, carboxylates, and acetylacetonates of main-group and transition metals with hydroperoxides and alcohols *Russ. J. Appl. Chem.* 2004, 72, 1987-1993.
- [8] Remizov, A. B.; Kamalova, D. I.; Skochilov, R. A.; Semenov, M. P. Self- and heteroassociates of cumyl hydroperoxide: FTIR-spectroscopy, chemometrics (factor analysis) and quantum chemical calculations. *Journal of Molecular Structure*. 2008, 880, 52-58.
- [9] Elgandy, E. M. The potential biologically active epoxide, hydroperoxide and endoperoxide derivatives derived from natural monoterpene β -myrcene. *Australian J. Basic and Applied Sciences*. 2008, 2, 221-224.
- [10] Krestov, G. A.; Novoselov, N. P.; Perelygin, I. S. Ionnaia Sol'vatatsia (Ion solvation); Nauka: Moskva, 1987.
- [11] Williams, D. H.; Westwel, M. S. Aspects of weak interactions *Chem. Soc. Rev.* 1998, 28, 57-63.