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MOLECULAR MODELING OF THE *TERT*-BUTYL HYDROPEROXIDE NMR ^{1}H AND ^{13}C SPECTRA

Keywords: NMR spectroscopy, tert-butyl hydroperoxide, chemical shift, magnetic shielding constant, GIAO, molecular modeling.

NMR ^{1}H and ^{13}C spectra of tert-butyl hydroperoxide in acetonitrile-d_3, chloroform-d and dimethyl sulfoxide-d_6 have been investigated by the NMR method. The calculation of magnetic shielding tensors and chemical shifts for ^{1}H and ^{13}C nuclei of the tert-butyl hydroperoxide molecule in the approximation of an isolated particle and considering the influence of the solvent in the framework of the continuum polarization model was carried out. Comparative analysis of experimental and computer NMR spectroscopy results revealed that the GIAO method with MP2/6-31G (d,p) level of theory and the PCM approach can be used to estimate the parameters of NMR ^{1}H and ^{13}C spectra of tert-butyl hydroperoxide.

Ключевые слова: ЯМР-спектроскопия, трет-бутилгидропероксид, химический сдвиг, константа магнитного экранирования, метод ГИАО, молекулярное моделирование.

Методом ЯМР ^{1}H и ^{13}C получены спектры трет-бутилгидропероксида в ацетонитриле-d_3, хлороформе-d и диметилсульфоксиде-d_6. В рамках модели поляризационного континуума проведен расчет тензоров магнитного экранирования и химических сдвигов для ядер ^{1}H и ^{13}C молекулы трет-бутилгидропероксида при приближении к изолированной частице и с учетом влияния растворителя. Сравнительный анализ экспериментальных и компьютерных результатов ЯМР-спектроскопии показал, что метод ГИАО с MP2/6-31G (d, p) уровнем теории и подходом PCM могут быть использованы для оценки параметров ЯМР ^{1}H и ^{13}C спектров трет -бутилгидропероксида.

Introduction

Quantum chemical methods are widely used for investigation the structural features of the organic peroxides and their associates with various classes of compounds, and to study the reactivity of hydroperoxides [1-4]. Computational chemistry is effective tool to get more structural information about peroxide bond activation by enzymes [5], transition metals compounds [6], amines and sulphide [3, 7], quaternary ammonium salts [1, 8]. The existing semi-empirical, ab initio and DFT - methods can reproduce the peroxides molecular geometry with sufficient accuracy [9]. Molecular modeling of the peroxide bond homolytic decomposition and hydroperoxides association processes is an additional information source of the structural effects that accompany these reactions. One of the criteria for the quantum-chemical method selection to study the hydroperoxides reactivity can be NMR ^{1}H and ^{13}C spectra parameters reproduction with sufficient accuracy. It should be noted that the parameters of the NMR spectra are very sensitive to slight changes in spatial and electronic structure of the molecule. The joint use of experimental and computational methods can be an information source of the structural features of the molecule caused by intra- and intermolecular interactions [10]. Calculations within the density functional theory (DFT) and perturbation theory (MP2) in the GIAO (Gauge Including Atomic Orbital) approximation for NMR spectra modeling of organic compounds are most often used, since they provided a good relationship between the computational cost and accuracy [10, 11].

The aim of this work is a substantiation of the method and basis for quantum-chemical calculation of the *tert*-butyl hydroperoxide NMR ^{1}H and ^{13}C spectra.

Experimental

Tert-butyl hydroperoxide ($(CH_3)_2C\text{-}O\text{-}OH$) was purified according to Ref. [12], its purity (99 %) was controlled by iodometry method. Experimental NMR ^{1}H and ^{13}C spectra of the hydroperoxide solutions were obtained by using the Bruker Avance II 400 spectrometer (NMR ^{1}H - 400 MHz, NMR ^{13}C – 100 MHz) at 298 K. Solvents – acetonitrile-d_3 (CD_3CN), chloroform-d ($CDCl_3$), and dimethyl sulfoxide-d_6 (DMSO-d_6) were Sigma-Aldrich reagents and used without additional purification but were stored above molecular sieves before using. Tetramethylsilane (TMS) was used as internal standard. The hydroperoxide concentration in solution was 0.03 mol·dm^{-3}.

Molecular geometry and electronic structure parameters, thermodynamic characteristics of the *tert*-butyl hydroperoxide molecule were calculated using the GAUSSIAN03 [13] software package. The hydroperoxide molecular geometry optimization and frequency harmonic vibrations calculation were carried out on the first step of investigations. The nature of the stationary points obtained was verified by calculating the vibrational frequencies at the same theory level.

To choose the optimal method for the $(CH_3)_2C\text{-}O\text{-}OH$ geometry calculation the hydroperoxide structure parameters were estimated by Hartree-Fock (HF), DFT (B3LYP and BHandHLYP) methods as well as on the MP2 theory level. The following basis sets were used in calculations: 6-31G, 6-31G(d), and 6-31G(d,p). The solvent effect was considered in the PCM approximation [14, 15]. The magnetic shielding tensors (χ, ppm) for ^{1}H and ^{13}C nuclei of the hydroperoxide molecule were calculated with the MP2/6-31G(d,p) and MP2/6-31G(d,p)/PCM optimized geometries by standard GIAO (Gauge-Independent Atomic Orbital) approach [16]. Optimization of the molecular geometry in the same approximation and calculation of magnetic shielding tensors in the framework of the GIAO approach were also performed for the TMS molecule. Obtained χ values for TMS (Table 1) were used for the hydroperoxide ^{1}H and ^{13}C nuclei chemical shifts calculations.

Table 1 - The magnetic shielding tensors for ^{1}H and ^{13}C nuclei of the tetramethylsilane molecule calculated within GIAO/MP2/6-31G(d,p) approach

Solvent	χ_H, ppm	χ_C, ppm
-	31.958	207.541
CH_3CN	31.952	207.925
$CHCl_3$	31.945	207.815
DMSO	31.940	207.858

Note: (χ vales are averaged over corresponding nuclei)

Inspecting the overall agreement between experimental and theoretical spectra RMS errors (σ) were used to consider the quality of the ^{1}H and ^{13}C nuclei chemical shifts calculations.

Results and discussions

Experimental NMR ^{1}H and ^{13}C spectra of tert-butyl hydroperoxide

Experimental NMR ^{1}H and ^{13}C studies of *tert*-butyl hydroperoxide were carried out in the following solvents: acetonitrile-d_3, chloroform-d and dimethyl sulfoxide-d_6 at 298 K. The concentration of the hydroperoxide in all samples was 0.03 mol·dm^{-3}. Tetramethylsilane was used as the internal standard. Parameters of the experimental NMR ^{1}H and ^{13}C spectra of the $(CH_3)_3C$-O-OH are listed in Table 2.

Table 2 - Experimental parameters of the tert-butyl hydroperoxide NMR ^{1}H and ^{13}C spectra

Solvent	ε [17]	δ (^{1}H), ppm.		δ (^{13}C), ppm	
		$-CH_3$	-COOH	$-CH_3$	-COOH
$CDCl_3$	4.8	1.27	7.24	25.71	80.87
CD_3CN	37.5	1.18	8.80	26.27	80.53
DMSO-d_6	46.7	1.12	10.73	26.01	76.56

Table 2 reveals the following features. The shift of the $-CH_3$ and-COOH groups signals in the NMR ^{1}H spectrum of the hydroperoxide with the solvent polarity increasing is observed. The signal of the hydroperoxide group proton appears at 7.24 ppm in chloroform-d, and in the more polar dimethyl sulfoxide-d_6 it was found at 10.73 ppm. When passing from $CDCl_3$ to DMSO-d_6 the signal of the $-CH_3$ groups protons are shifted to the strong field. Another effect is observed in the case of the NMR ^{13}C spectrum, the signal of a tertiary carbon atom is shifted to a strong field on 4.34 ppm in DMSO-d_6 as compared to $CDCl_3$.

Equilibrium configuration of the tert-butyl hydroperoxide in the HF, MP2, and DFT methods approximation

The first step of the $(CH_3)_3C$-O-OH NMR spectra calculatuion was the estimation of the hydroperoxide molecular geometry parameters and electronic structure to choose method and basis set for the further investigations. The $(CH_3)_3C$-O-OH molecular geometry optimization was carried out by HF, DFT (B3LYP и BHandHLYP) and MP2 methods, the following basis sets were used in calculations: 6-31G, 6-31G(d), and 6-31G(d,p). Peroxide bond O-O is a reaction centre in this type of chemical initiators thus the main attention was focused on the geometry of -CO-OH fragment. Table 3 illustrates the influence of theory level as well as basis set on the -CO-OH fragment geometry parameters. The calculation results were compared with experimental values [18]. The best agreement between calculated and experimental parameters can be seen in the case of MP2/6-31G(d,p) method. Thus it was used in the further calculations.

Table 3 - Molecular geometry parameters of -COOH moiety of the tert-butyl hydroperoxide molecule

Method/ basis set	Bond length, Å			Angle, °		
	C–O	O–O	O–H	COO	OOH	COOH
HF/6-31G	1.464	1.459	0.954	108.8	101.2	166.9
HF/6-31G (d)	1.426	1.393	0.948	110.3	101.9	117.6
HF/6-31G (d,p)	1.426	1.394	0.945	110.2	102.3	115.9
B3LYP/ 6-31G	1.489	1.529	0.984	107.7	98.4	134.4
B3LYP/ 6-31G(d)	1.450	1.457	0.973	109.2	99.7	110.9
B3LYP/ 6-31G(d,p)	1.450	1.458	0.971	109.1	99.8	110.7
BHandHLYP/6-31G	1.468	1.487	0.968	107.8	99.8	144.7
BHandHLYP/6-31G(d)	1.431	1.419	0.960	109.4	100.9	113.4
BHandHLYP/6-31G(d,p)	1.432	1.419	0.957	109.3	101.0	113.4
MP2/6-31G	1.501	1.575	0.988	106.3	95.5	152.5
MP2/6-31G(d)	1.448	1.472	0.977	108.0	98.2	116.8
MP2/6-31G(d,p)	1.446	1.473	0.970	107.7	98.2	114.7
Experiment [18]	1.443	1.473	0.990	109.6	100.0	114.0

Calculations with solvent effect accounting were al so carried out for the $(CH_3)_3C$-O-OH molecule by MP2/6-31G(d,p) method within PCM approximation. Obtained geometry parameters are listed in Table 4. The solvent does not affect the O-O bond length. Solvent effect is noticeable for O-H and C-O bonds, O-O-H and C-O-O bond angles, and C-O-O-H torsion angle. Significant changes of O-H and C-O bonds, O-O-H and C-O-O bond angles are observed in the case of CH_3CN and DMSO, while $CHCl_3$ has less influence.

Table 4 - Molecular geometry parameters of the tert-butyl hydroperoxide molecule calculated within MP2/6-31G(d,p)/PCM approximation

Parameter	Solvent			
	-	CH_3CN	$CHCl_3$	DMSO
r_{O-O},Å	1.473	1.472	1.472	1.472
r_{O-H},Å	0.970	0.986	0.980	0.986
r_{C-O},Å	1.446	1.450	1.449	1.450
∠O-O-H,°	98.2	99.4	98.9	99.3
∠C-O-O, °	107.7	108.2	107.9	108.1
∠C-O-O-H, °	114.7	113.7	116.3	114.5

Thus MP2/6-31G(d,p) and PCM/MP2/6-31G(d,p) equilibrium configuration of the *tert*-butyl hydroperoxide will be used for the further calculations.

GIAO NMR ^{1}H and ^{13}C spectra of the tert-butyl hydroperoxide

With regard to the results obtained from this foregoing study, the GIAO calculations for the *tert*-butyl hydroperoxide molecule were performed at MP2/6-31G(d,p) level of theory in the approximation of the isolated molecule as well as with solvent effect accounting within PCM approach. Fig. 1 illustrates the structural model of the *tert*-butyl hydroperoxide molecule (equilibrium configuration obtained at MP2/6-31G(d,p) level of theory) with atom numbering used for GIAO NMR ^{1}H and ^{13}C spectra parameters representation.

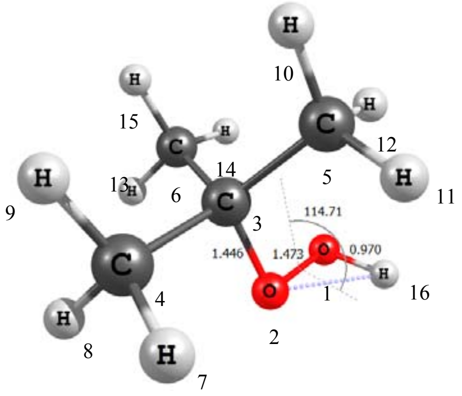

Fig. 1 - Tert-butyl hydroperoxide structural model with corresponding atom numbering (MP2/6-31G(d,p))

To estimate the hydroperoxide NMR ^{1}H and ^{13}C spectra parameters the magnetic shielding constants (χ, ppm) for corresponding nuclei were calculated by GIAO method. Obtained χ values for magnetically equivalent nuclei were averaged and listed in Table 5. On the base of the obtained χ values the chemical shift values (δ, ppm) of the ^{1}H and ^{13}C nuclei in the hydroperoxide molecule were evaluated. TMS was used as standard, for which the molecular geometry optimization and χ calculation were performed using the same level of theory and basis set. Values of the ^{1}H and ^{13}C chemical shifts were found as the difference of the magnetic shielding tensors of the corresponding TMS and hydroperoxide nuclei.

For the MP2/6-31G(d,p) calculated ^{1}H and ^{13}C chemical shifts there was no full conformity with the experimental data. Experimental δ values for -CO-OH moiety proton in all solvents are higher than the δ = 6.805 ppm calculated in the isolated molecule approximation. The labile protons signals are usually shifted to lower field in DMSO-d_6 solution. Difference between δ values of -CO-OH moiety proton for CH_3CN and $CHCl_3$ solutions may also be due to the influence of the solvent. Formation of hydroperoxides self-associates are possible in the low-polarity solvents [19] that may affect the magnitude of the proton chemical shift of the -CO-OH fragment.

Fig. 2 presents one of many possible configurations of the *tert*-butyl hydroperoxide molecule dimer. Molecular geometry optimization of this homoassociate was performed at MP2/6-31G(d,p) theory level without solvent effect accounting. This associate is stabilized by the formation of two intermolecular hydrogen bonds: O…HO distance is 1.834 Å, bond angle O…H-O – 161.51°, O-H bond length increases up to 0.982 Å. However, the configuration of the hydroperoxide fragment is not largely changed. For this associate χ values were calculated of by GIAO method (MP2/6-31G(d,p) theory level, isolated molecule approximation) and the chemical shift values of the ^{1}H and ^{13}C nuclei were evaluated. The δ value of 10.541 ppm has been obtained for the -CO-OH moiety proton. This is significantly higher than the experimental values observed in chloroform-d and acetonitrile-d_3 solutions.

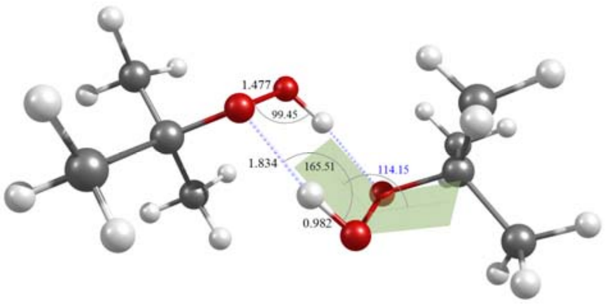

Fig. 2 - Structural model of the tert-butyl hydroperoxide dimer (MP2/6-31G(d,p))

Study the hydroperoxide concentration effect on the signals position in the NMR ^{1}H spectrum in CD_3CN and $CDCl_3$ solutions has been carried out. The hydroperoxide concentration was ranged within (2.1·– 500.0)·10^{-3} и (9.0 – 20.0)·10^{-3} mol·dm^{-3} in CD_3CN and $CDCl_3$ respectively. Changing in the hydroperoxide concentration in these ranges does not lead to a change in the signal position in the spectrum. Hence, the chemical shift of the hydroperoxide group proton is independent of the hydroperoxide concentration in the system in experimental conditions. Thus, calculation and NMR ^{1}H spectroscopy results showed that the hydroperoxide dimers do not formed in the system. And observed chemical shift values for the -CO-OH moiety proton are due to the solvent effect. In order to account for the solvent effect in the calculation of magnetic shielding tensors the PCM approach was used. Magnetic shielding tensors for ^{1}H and ^{13}C nuclei of the *tert*-butyl hydroperoxide, calculated by GIAO method at MP2/6-31G(d,p) theory level with PCM solvent effect (Tables 5 and 6) have been used for the chemical shift values of the ^{1}H and ^{13}C nuclei estimation.

Table 6 illustrates the chemical shift values (δ, ppm) for ^{1}H and ^{13}C nuclei of the *tert*-butyl hydroperoxide, calculated at MP2/6-31G(d,p) level of theory with solvent effect accounting.

Table 5 - GIAO-magnetic shielding tensors for ^{1}H and ^{13}C nuclei of the tert-butyl hydroperoxide, calculated at MP2/6-31G(d,p) theory level

Sol vent	NMR ^{1}H				NMR ^{13}C			
	-COOH		-CH$_3$		-COOH		-CH$_3$	
	χ, ppm	δ, ppm	χ, ppm	δ, ppm	χ, ppm	δ, ppm	χ, ppm	δ, ppm
-	25.15	6.805	30.73	1.226	128.16	79.379	180.38	27.163
CH$_3$CN	23.18	8.771	30.70	1.250	127.61	80.311	180.47	27.455
CHCl$_3$	23.82	8.136	30.71	1.243	127.84	79.977	180.42	27.394
DMSO	23.16	8.778	30.70	1.238	127.64	80.219	180.47	27.391

Table 6 - GIAO chemical shifts of the ^{1}H and ^{13}C nuclei of the tert-butyl hydroperoxide (MP2/6-31G(d,p)/PCM)

Atom	CH$_3$CN			CHCl$_3$		
	1	2	Δ	1	2	Δ
δ, ppm NMR ^{13}C						
C$_3$	80.31	80.53	0.22	79.98	80.87	0.89
C$_4$	27.94	26.27	1.67	27.90	25.71	2.19
C$_5$	27.11	26.27	0.84	27.21	25.71	1.50
C$_6$	27.30	26.27	1.03	27.00	25.71	1.29
σ	1.15			2.38		
δ, ppm NMR ^{1}H						
H$_7$	1.06	1.18	0.12	1.04	1.27	0.23
H$_8$	1.08	1.18	0.10	1.10	1.27	0.17
H$_9$	1.17	1.18	0.01	1.10	1.27	0.17
H$_{10}$	1.00	1.18	0.18	0.96	1.27	0.31
H$_{11}$	1.09	1.18	0.09	1.06	1.27	0.21
H$_{12}$	1.93	1.18	0.75	1.93	1.27	0.66
H$_{13}$	1.07	1.18	0.11	1.10	1.27	0.17
H$_{14}$	1.95	1.18	0.77	1.90	1.27	0.63
H$_{15}$	0.93	1.18	0.25	0.89	1.27	0.38
H$_{16}$	8.78	8.80	0.02	8.13	7.24	0.89
σ	0.13			0.20		

Atom	DMSO		
	1	2	Δ
δ, ppm NMR ^{13}C			
C$_3$	80.22	76.56	3.66
C$_4$	27.88	26.01	1.88
C$_5$	27.07	26.01	1.06
C$_6$	27.22	26.01	1.21
σ	4.88		
δ, ppm NMR ^{1}H			

Atom	CH$_3$CN			CHCl$_3$		
	1	2	Δ	1	2	Δ
H$_7$	1.05	1.12	0.07			
H$_8$	1.07	1.12	0.05			
H$_9$	1.14	1.12	0.02			
H$_{10}$	0.98	1.12	0.14			
H$_{11}$	1.07	1.12	0.05			
H$_{12}$	1.92	1.12	0.80			
H$_{13}$	1.05	1.12	0.07			
H$_{14}$	1.93	1.12	0.81			
H$_{15}$	0.91	1.12	0.21			
H$_{16}$	8.77	10.73	1.96			
σ	0.52					

Notes: 1 – calculated, 2 – experimental; Δ – difference between the experimental and calculated hydroperoxide chemical shifts; σ – RMS errors.

Concerning the spectral patterns of a -CH$_3$ group protons, inspection of Tables 5 and 6 reveals the following features: the pattern of NMR ^{1}H spectra of (CH$_3$)$_3$C-O-OH is rather correctly reproduced at selected computational level for all solvents; the best agreement between the experimental and calculated ^{1}H and ^{13}C chemical shifts of the -CO-OH moiety is observed for acetonitrile-d solution; for all cases solvent effect accounting leads to a better result compared to the isolated molecule approximation; calculated and experimental values of δ for -CO-OH group proton decrease symbatically with the solvent polarity increasing. But in DMSO-d$_6$ solution a significant shift to lower field region is observed for -CO-OH group proton as compared with other solvents. Calculated δ value for this proton in DMSO is very close to the experimentally observed one in acetonitrile-d$_3$ solution. This shift can be explained by the formation of hydroperoxide-DMSO-d$_6$ heteroassociates in experimental conditions. One should note that similar values of $\delta = 10.77 \div 10.33$ ppm has a -CO-OH group proton of *tert*-butyl hydroperoxide complex-bonded with tetraalkylammonium bromides [20].

Conclusions

The influence of the solvent on the NMR spectra parameters the of *tert*-butyl hydroperoxide was investigated. It is shown that with increasing polarity of the solvent signal of the hydroperoxide group proton shifts toward weak fields. On the basis of the complex data analysis of the spectroscopic studies and molecular modeling shows that the GIAO method with the MP2/6-31G (d,p) level of theory and the PCM approximation can be used to estimate NMR ^{1}H and ^{13}C spectra parameters of *tert*-butyl hydroperoxide.

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