ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 1, pp. 16–17. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © N.A. Turovskij, E.V. Raksha, Yu.V. Berestneva, M.Yu. Zubritskij, 2014, published in Zhurnal Obshchei Khimii, 2014, Vol. 84, No. 1, pp. 18–19.

Formation of 1,1,3-Trimethyl-3-(4-methylphenyl)butyl Hydroperoxide Complex with Tetrabutylammonium Bromide

N. A. Turovskij[a], E. V. Raksha[a], Yu. V. Berestneva[a], and M. Yu. Zubritskij[b]

[a] *Donetsk National University, ul. Universitetskaya 24, Donetsk, 83001 Ukraine*
e-mail: N.Turovskij@donnu.edu.ua

[b] *Litvinenko Institute of Physico-Organic Chemistry and Coal Chemistry, National Academy of Sciences of Ukraine, Donetsk, Ukraine*

Received April 18, 2013

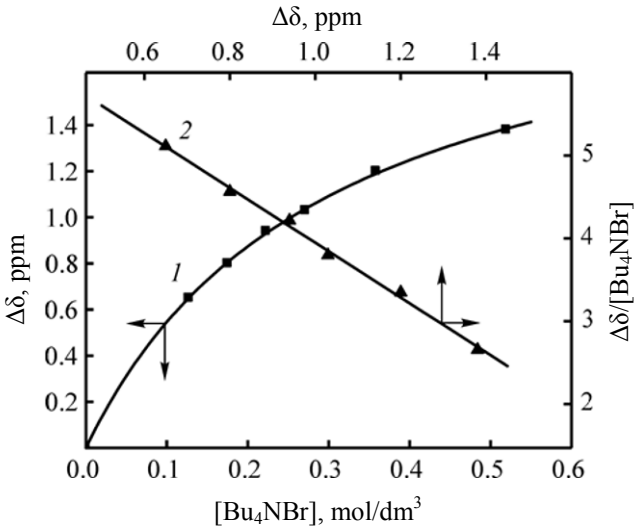
Abstract—The interaction of 1,1,3-trimethyl-3-(4-methylphenyl)butyl peroxide with tetrabutylammonium bromide has been studied by means of ^{1}H NMR spectroscopy. The complex formation between the reacting species has been confirmed, its equilibrium constant being K = (3.01±0.09) L/mol at 294 K.

DOI: 10.1134/S1070363214010046

Hydroperoxides are efficient chemical sources of the free radicals for oxidative modification of organic compounds. Quaternary ammonium salts are known to catalyze radical decomposition of hydroperoxides [1, 2], thus favoring the liquid-phase oxidation of hydrocarbons with molecular oxygen under milder conditions [3, 4]. The kinetic studies have revealed that the ammonium salts catalysis of hydroperoxides decomposition included the stage of intermediate complex formation [1, 2, 4]. The possible structures of hydroperoxide-ammonium salt complexes have been suggested basing on the molecular modeling results [2, 4].

This work aimed to experimentally confirm the complex formation upon interaction of 1,1,3-trimethyl-3-(4-methylphenyl)butyl hydroperoxide (**I**) with tetrabutylammonium bromide at 294 K by ^{1}H NMR. Under the above-stated conditions, the rate of the hydroperoxide I decay was negligibly low. The rate constant of thermolysis of I in acetonitrile solution was of 7×10^{-12} s^{-1} [5].

In the ^{1}H NMR spectrum of **I**, the signals at 0.86, 1.34, and 2.29 ppm were assigned to methyl groups protons, the signal at 2.03 ppm corresponded to methylene protons, the signals of benzene ring protons were observed at 7.10 and 7.30 ppm, and the signal at 8.53 ppm was assigned to the hydroperoxide group protons. Variation of concentration of **I** within the 0.01–0.05 mol/L range did not lead to any spectral changes. However, the addition of Bu_4NBr shifted the signal of hydroperoxide group downfield without its broadening. ^{1}H NMR studies were performed in the excess of the quaternary ammonium salt. Concentration of the hydroperoxide **I** was always constant and equaled 0.03 mol/L, whereas the Bu_4NBr concentration was varied within 0.14–0.57 mol/L. With increasing Bu_4NBr concentration, the downfield shift



Chemical shift of hydroperoxide group proton of 1,1,3-trimethyl-3-(4-methylphenyl)butyl hydroperoxide as function of Bu_4NBr concentration in direct coordinates (*1*) and in the Foster–Fyfe coordinates (*2*) ([ROOH] = 0.03 mol/L, 294 K, in acetonitrile-d_3).

of hydroperoxide signal was enhanced. The changes of the hydroperoxide proton signal were typical of complex formation between **I** and Bu_4NBr under conditions of fast proton exchange between the free and the bonded COOH groups. Hence, in the case of the **I**–Bu_4NBr system, the COOH chemical shift (δ) was an averaged signal of the free peroxide groups (δ_{ROOH}) and the peroxide groups bonded into complex (δ_{comp}).

The hydroperoxide chemical shift change ($\Delta\delta = \delta - \delta_{ROOH}$) as function of Bu_4NBr was not linear (see figure). In the excess of Bu_4NBr, assuming the 1 : 1 complex formation, the obtained data could be analyzed by fitting with the Foster–Fyfe equation [6].

$$\Delta\delta/[Bu_4NBr] = -K\Delta\delta + K\Delta\delta_{max}$$

In the equation, K is the equilibrium constant of the complex formation, Δδ is the change of the chemical shift in the presence of certain concentration of the ammonium salt, $[Bu_4NBr]$, and $\Delta\delta_{max}$ is the difference between the chemical shifts of the free and the bonded hydroperoxide ($\Delta\delta_{max} = \delta_{comp} - \delta_{ROOH}$).

In the Foster–Fyfe coordinates, the experimental data could be fitted with a linear function with K = 3.01±0.09 L/mol and the chemical shift of the bonded hydroperoxide proton of δ_{comp} = 10.72±0.04 ppm.

As the signals of methyl and methylene protons of Bu_4NBr were not changed upon the complex formation, the cation did not interact directly with the peroxide. The complex formation should thus have been due to the hydrogen bonding between bromide anion and COOH group of the hydroperoxide.

EXPERIMENTAL

^1H NMR studies of the solutions in acetonitrile-d_3 were performed using Bruker Avance II 400 spectrometer (400 MHz, 294 K, TMS as internal standard).

1,1,3-Trimethyl-3-(4-methylphenyl)butyl hydroperoxide preparation method and its properties were reported in [7]. The hydroperoxide was purified as described in [8], its purity was of 99.8% as checked by iodometry. Tetrabutylammonium bromide was purified via double precipitation from its acetonitrile solution with excess of diethyl ether. The salt purity was of 99.8% as determined by argentometry with potentiometric fixation of the equivalence point. Bu_4NBr was then stored in a box drained with P_2O_5.

REFERENCES

1. Turovskii, N.A., Antonovskii, V.L., Opeida, I.A., Nikolaevskii, A.N., and Shufletyuk, V.I., *Khim. Fiz*., 2001, vol. 20, no. 2, p. 41.
2. Turovskii, N.A., Raksha, E.V.,Gevus, O.I., Opeida, I.A., and Zaikov, G.E., *Oxidation Commun*., 2009, vol. 32, no. 1, p. 69.
3. Matienko, L.I., Mosolova, L.A., and Zaikov, G.E., *Russ. Chem. Rev*., 2009, vol. 78, no. 3, p. 211.
4. Turovsky, M.A., Opeida, I.A., Turovskaya, E.N., Raksha, O.V., Kuznetsova, N.O., and Zaikov, G.E., *Oxidation Commun*., 2006, vol. 29, no. 2, p. 249.
5. Turovsky, M.A., Raksha, O.V., Opeida, I.A., and Turovska, O.M., *Oxidation Commun*., 2007, vol. 30, no. 3, p. 504.
6. Fielding, L., *Tetrahedron*, 2000, vol. 56, p. 6151.
7. Kinash, N.I. and Vostres, V.B., *Visn. Nats. Univ. "L'vivs'ka Politekhnika,"* 2005, no. 529, p. 124.
8. Hock, H. and Lang, S., *Chem. Ber.,* 1944, vol. 77, nos. 3–4, p. 257.