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ScienceDirect
Journal of Molecular Structure 880 (2008) 52–58
Journal of MOLECULAR STRUCTURE
www.elsevier.com/locate/molstruc

Self- and heteroassociates of cumyl hydroperoxide: FTIR-spectroscopy, chemometrics (factor analysis) and quantum chemical calculations

A.B. Remizov [a], D.I. Kamalova [b,*], R.A. Skochilov [a], M.P. Semenov [a]

[a] *Kazan State Technological University, Karl Marx Street, 68, Kazan 420015, Russia*
[b] *Kazan State University, Department of Physics, Kremlevskaya Street, 18, Kazan 420008, Russia*

Received 9 October 2007; received in revised form 27 November 2007; accepted 30 November 2007
Available online 8 December 2007

Abstract

Self- and heteroassociation of cumyl hydroperoxide and acetophenone in *n*-decane solutions were studied by FTIR spectroscopy (3100–3700 cm^{-1}, 298–358 K). To interpret spectroscopic data, the new approach of factor analysis was offered. Equilibrium constants and thermodynamic parameters of associate formation were determined. The DFT calculations of cumyl hydroperoxide conformations, their self- and heteroassociates were carried out.

Keywords: Hydrogen bond; Infrared spectra; Conformation; Factor analysis; DFT calculation

1. Introduction

Decay of hydroperoxides is one of the major stages of liquid-phase oxidation of hydrocarbons, it influences on a speed of the process on the whole [1]. Association and self-association play an important part when hydroperoxides decay in solutions. So, these phenomena are objects of many theoretical and experimental investigations [2,3]. Cumyl hydroperoxide ($C_6H_5(CH_3)_2COOH$) (CUH) is a primary product of cumene oxidation during production of phenol and acetone. Acetophenone ($C_6H_5C({=}O)CH_3$) (AP) is the by-product in this process.

Earlier, we investigated self-association of CUH in various solvents [4,5]. The technique of determination of individual spectra and concentration of associates was offered by use of the factor analysis in Ref. [5]. In the present work, this technique has been developed and applied for IR spectroscopic study of association of CUH with AP.

Besides, the quantum chemical DFT calculations of cumyl hydroperoxide conformations and their self- and heteroassociates are carried out. The calculational results are compared to the results of IR spectroscopic study and factor analysis.

2. Experimental and computational methods

The concentration of liquid CUH was 6.785 mol l^{-1}. CUH was purified through its sodium salt by the procedure described in Ref. [6]. *n*-Decane (*n*-$C_{10}H_{22}$) was used as a solvent. Solutions' concentrations of CUH with AP were determined iodometrically. The IR spectra in stretching vibrations region of O—H group (3100–3700 cm^{-1}) were recorded with Perkin-Elmer Spectrum 100 FTIR spectrometer. The spectra were normalized on the cell thickness. Temperature effects on the IR spectra at 298–358 K were studied with the use of standard cells maintained by thermostat. The temperature accuracy was ±0.3 K. An initial concentration of CUH or AP was varied. The IR spectra were analyzed by the factor analysis techniques.

The quantum chemical calculations were carried out by use of Gaussian 98 program [7]. We optimized each molecular system geometry using B3LYP density functional theory with 6-31G(d,p) and 6-311++G(df,p) basis sets. We carried out the total geometry optimization of molecular system with calculation of vibration frequencies without a

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[*] Corresponding author. Tel.: +7 843 2315 214.
E-mail address: dina.kamalova@ksu.ru (D.I. Kamalova).

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doi:10.1016/j.molstruc.2007.11.047