Journal of Molecular Structure 972 (2010) 104–110

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Hydrogen bonds in self- and heteroassociates of cumyl hydroperoxide in solutions and polymeric matrixes

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ARTICLE INFO

Article history:
Received 20 October 2009
Received in revised form 28 January 2010
Accepted 2 February 2010
Available online 6 February 2010

Keywords:
Hydrogen bond
Infrared spectra
Conformation
Factor analysis
DFT calculation

ABSTRACT

Self- and heteroassociation of cumyl hydroperoxide hydrogen bonded with acetone, acetophenone and acetonitrile as a proton acceptor in *n*-decane solutions was studied by FTIR spectroscopy in the range of 3100–3700 cm^{-1}. The hydrogen bonds of cumyl hydroperoxide were investigated in both benzene and two polymeric matrixes. To interpret spectroscopic data the factor analysis was used. Equilibrium constants and thermodynamic parameters of the heteroassociate formation were determined. The DFT calculations of self- and heteroassociates of cumyl hydroperoxide were carried out.

1. Introduction

IR-spectroscopy is one of the main methods of hydrogen bond study. The use of FTIR spectroscopy combined with the factor analysis (FA) and quantum chemical calculations allows one to define the structure of the most stable conformations and associates of molecules. We continue to study the H-bonded association of cumyl hydroperoxide ($C_6H_5(CH_3)_2COOH$) (CUH) [1,2]. Earlier, we investigated the self-association of CUH and the formation of dimers [1,2]. By using FA we have offered the technique of determination of individual spectra and concentrations of associates [1]. In the present work we have been investigated the solutions of CUH with the concentration from 0.15 to 0.22 mol l^{-1}. In this case the trimers of CUH appear in the solutions. Besides, the study of heteroassociates of cumyl hydroperoxides with acetone ($(CH_3)_2C{=}O$) (AC), acetophenone ($C_6H_5C({=}O)CH_3$) (AP) and acetonitrile ($(CH_3)C{\equiv}N$) (AN) as a proton acceptor has been carried out. The quantum chemical calculations (DFT) of the trimers of CUH, the heteroassociates CUH + AC, CUH + AP and CUH + AN were performed too.

2. Experimental and computational methods

The concentration of liquid CUH in solutions varied in the range of 0.01–0.22 mol l^{-1}. CUH was purified through its sodium salt by the procedure described in Ref. [3]. *n*-Decane (*n*-$C_{10}H_{22}$) was used as a solvent. Acetone (AC), acetophenone (AP) and acetonitrile (AN) were as proton acceptors. The FTIR spectra were recorded with Perkin–Elmer Spectrum 100 FTIR spectrometer. The spectra were normalized on the cell thickness. The IR spectra were studied at the different temperatures in the range of 25–85 °C with the use of standard thermostat cells. The IR spectra were analyzed by FA techniques [1,2,4].

The quantum chemical calculations were carried out by use of Gaussian 98 program [5]. We optimized molecular system geometry by 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 scaling multiplier. Stability of different associates was verified by the absence of the negative calculated vibrational frequencies.

3. Results and discussion

FTIR absorption spectra of CUH + AC solutions in the region of 3300–3600 cm^{-1} in *n*-decane at 25 and 70 °C are represented in Fig. 1. In the spectra of CUH ($C \sim 0.01$ mol l^{-1}) the doublet at 3521 and 3558 cm^{-1} concerned with OH-vibration of different conformations of free CUH molecules is observed [6]. The intensity of the absorption band at 3429 cm^{-1} assigned to the overtone of C=O stretching vibration of free AC molecules and the intensity of the broad band at 3376 cm^{-1} assigned to both self- and heteroassociates change when the total solution's concentration varies (Fig. 1). The presence of the wide absorption bands and the narrow

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doi:10.1016/j.molstruc.2010.02.002