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Journal of Molecular Structure 700 (2004) 73–79
Journal of MOLECULAR STRUCTURE
www.elsevier.com/locate/molstruc

FT-IR study of self-association of some hydroperoxides

A.B. Remizov[a], D.I. Kamalova[b,*], R.A. Skochilov[a], I.A. Suvorova[a], N.N. Batyrshin[a], Kh.E. Kharlampidi[a]

[a]*Kazan State Technological University, Karl Marx St. 68, Kazan 420015, Russia*
[b]*Kazan State University, Kremlevskaya St. 18, Kazan 420008, Russia*

Received 17 November 2003; accepted 22 December 2003

Abstract

Self-association of cumyl, tertiary butyl and 3-phenylmethyl hydroperoxides in solutions of *n*-decane, carbon tetrachloride and chlorobenzene were studied by IR spectroscopy (3100–3700 cm^{-1}, 293–353 K). The experimental data were interpreted by factor analysis and band contour resolution. The di- and trimerization constants and thermodynamic parameters of self-associates were determined. Intramolecular hydrogen bond of cumyl hydroperoxide was investigated. The conformations of tertiary butyl and cumyl hydroperoxides were studied. The solvent influence on the thermodynamic parameters of hydrogen bond was found.

Keywords: Hydrogen bond; Infrared spectra; Conformation; Factor analysis; Band resolution

1. Introduction

The study of association of hydroperoxides allows us to estimate more conclusively the results obtained in liquid-phase oxidation of hydrocarbons and predict a way to radically improve this process [1,2]. The equilibrium constants and energies of association of hydrocarbon peroxides were obtained for the first time in studying the IR spectra of solutions of tertiary butyl hydroperoxide $(CH_3)_3COOH$ (TBH). Later, the self-association of cumyl hydroperoxide $C_6H_5C(CH_3)_2OOH$ (CUH), TBH and 3-phenylmethyl hydroperoxide $(C_6H_5)_3COOH$ (PMH) was investigated by NMR and IR spectroscopy. The intramolecular hydrogen bond in CUH was studied by IR spectroscopy (see Refs. in Ref. [3]). However, the band contour resolution of digitized infrared spectra and mathematical technique of factor analysis were not used. No information about self-association of hydroperoxides in solutions of CUH in saturated hydrocarbons was obtained. Until now there are no data on the conformations of PMH and internal rotation in CUH was not sufficiently taken into account.

In this work, IR spectroscopy is applied to study the internal rotation and the association of TBH, CUH and PMH in solutions in *n*-decane, carbon tetrachloride and chlorobenzene.

2. Experimental

The concentrations of liquid TBH and CUH were 9.92 and 6.785 mol l^{-1}, respectively. CUH was purified through its sodium salt by the procedure described in Ref. [4]. PMH was synthesized by the method [5].

The IR spectra were recorded with Bruker 22 Vector spectrometer. Solutions' concentrations were determined iodometrically. The spectral slit width was of the order of 1.5–2 cm^{-1}. The wide of the narrowest bands were ~10 cm^{-1}, so instrumental distortions of band contours were not taken into account. Temperature effects on the IR spectra at 293–358 K were studied with the use of standard cells maintained at a constant temperature accurate to ±0.3 K.

The IR spectra were analyzed by factor analysis techniques combined with decomposition of experimental spectral contours into analytic contours.

* Corresponding author. Tel.: +7-8432-315-173.
E-mail address: dina.kamalova@ksu.ru (D.I. Kamalova).

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doi:10.1016/j.molstruc.2003.12.051