Cryosolution infrared study of hydrogen bonded halothane acetylene complex

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A B S T R A C T

The interactions between halothane (2-bromo-2-chloro-1,1,1-trifluoroethane) and acetylene (C_2H_2) are studied by FTIR spectroscopy. Results obtained in liquid cryosolutions in Kr suggest weak complex formation stabilized by H − bond. The complexation enthalpy (~11 kJ/mol) is evaluated in a series of temperature measurements (T ~ 120−160 K) of integrated intensity of selected bands performed in liquefied Kr. The quantum chemical MP2/6-311++G(2d,2p) calculations predict four different structures of the complex. The most stable and populated (94% at T~120 K) structure corresponds to the H − bond between H atom of halothane and pi-electron of triple bond between C atoms of acetylene. Wave numbers of vibrational bands of the most stable structure are calculated in anharmonic approximation implemented in Gaussian program.

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1. Introduction

Halothane ($C_2HBrClF_3$) belongs to a group of general anesthetics which act predominantly by perturbing intermolecular interactions such as van der Waals or hydrogen bonding without breaking or forming covalent bonds. Numerous ab initio calculations predict two conformers of halothane. However, only the staggered structure of halothane corresponds to the minimum on the potential energy surface. Whereas the eclipsed structure belongs to a first order saddle point. This is true for the gas phase and non polar liquid solutions. The CH group can play the role of a weak donor in interactions with molecules containing electron lone pairs or reach electron density region. Often such CH donors reveal unusual spectroscopic properties. Namely the CH stretching vibration shows a blue shift in the case of interactions with particular acceptors [1−4]. Halothane exhibits the blue shift effect in mixtures with methyl fluoride (FCH_3, FCD_3) [5]. However, contrary to fluoroform, halothane forms "red shifting" H − bonds with such oxygen containing acceptors as dimethyl ether [6] and acetone [7]. Recent attention has been focused on the features of interactions between halothane and pi electron systems as C_2H_4, benzene [8,9]. It is supposed that such a type of interaction is responsible for

anesthetic action of halothane.

In this report, we present the results on the cryospectroscopic temperature studies of interactions between halothane and acetylene, with pi electron system localized in the vicinity of triple C≡C bond. Ab initio calculations are made to find local minima which correspond to stable structures. Option "freq = anahrm" has been used to obtain spectroscopic parameters of the most stable structure.

2. Experimental and computational methods

The experimental setups for temperature measurements were close to that presented earlier [7,10]. The FTIR spectra of cryosolutions of halothane + acetylene in liquefied Kr (T ~ 120−160 K) are studied in the frequency domain of c.a. 800 ÷ 7000 cm^{-1} using a Nicolet 6700 Fourier Transform spectrometer, with a resolution of 0.5 cm^{-1}. Relatively small concentrations ~10^{17}−10^{18} molecules/cm^3 of halothane and acetylene were used for spectroscopic measurements in the region of fundamental bands. Overtone bands ($2\nu(CH)$) were registered with noticeably larger concentrations of an order of ~10^{19} molecules/cm^3. The formation enthalpy (ΔH) was evaluated by studying the behavior of selected bands of monomers and of complex as a function of temperature. A small correction on the temperature change of the Kr density (~0.6 kJ/mol) was taken into account [11]. The data were averaged over a set of measurements.

The experimental data are interpreted in comparison, with the results of quantum chemical calculation. Theoretical calculations were run using the GAUSSIAN 09 Rev. D.01 package [12]. The local minima of $C_2HBrClF_3 + C_2H_2$ system were searched starting from several initial configurations. The local minimum found was fully optimized using ab initio second order Møller-Plesset perturbation (MP2) frozen core method [13] with a set of the Pople type basis sets. The final basis set (6-311++G(2d,2p)) have been chosen as a compromise between the accuracy of calculations and available computing resources. The equilibrium geometries, interaction energies and harmonic vibrational wave numbers of the complexes were obtained using CP-corrected gradient techniques [14,15]. The structures were characterized as those local minima having all real wave numbers. To improve the comparison procedure between experimental and theoretical spectra, the spectroscopic parameters of the most populated form of $C_2HBrClF_3 \cdot C_2H_2$ complex have been calculated using the option "freq = anharm" [16]. The AIM2000 program [17,18] was used to analyze the topology of the electron density in the vicinity of the bond critical points (BCP).

3. Results of measurements

Fig. 1 shows typical example of the extraction of the bond ascribed to a complex $C_2HBrClF_3 \cdot C_2H_2$ in the region of CH stretching vibrations of halothane and acetylene. The band attributed to the CH stretch of halothane in the complex is red shifted with respect to the monomer band by c.a. -4.2 cm^{-1}. The integrated intensity of this band decreases with increasing temperature of the mixture, as it is presented in Fig. 2. Numerous concentration and temperature measurements suggest that the absolute integrated intensity of the CH stretch of halothane noticeably increases due to the complex formation. The results obtained in the temperature range of ~120−160 K were used to evaluate the formation enthalpy. An example of van't Hoff plot is shown in Fig. 3. The formation enthalpy evaluated over a set of measurements and
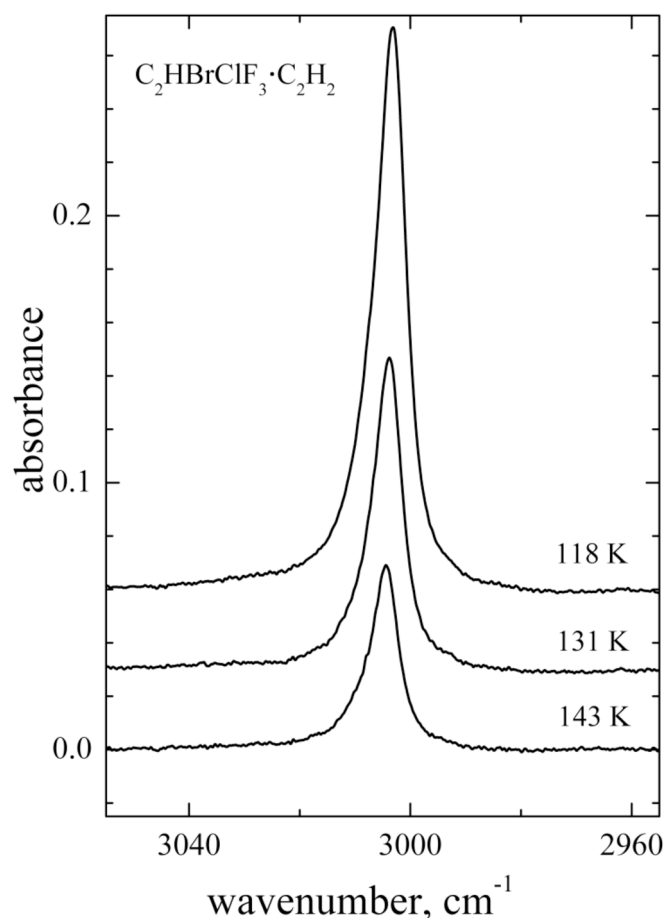

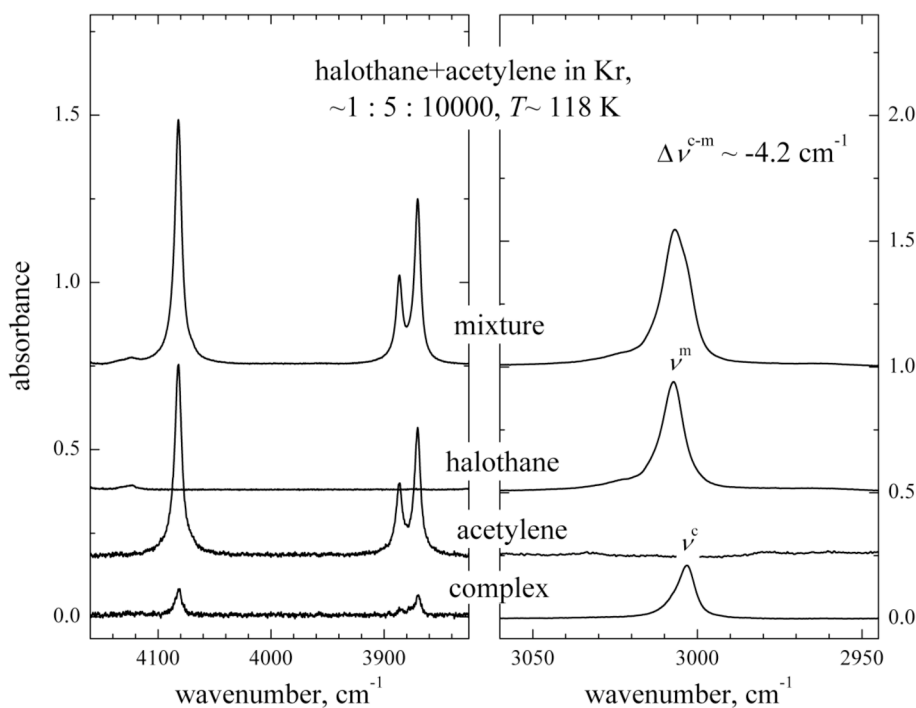**Fig. 2.** Typical temperature change of the ν(CH) band of halothane in $C_2HBrClF_3 \cdot C_2H_2$ complex.

Fig. 1. The IR spectrum of halothane + acetylene mixture in liquefied Kr at $T = 118$ K. Left panel − the region of combination bands of acetylene ($\nu_3 + \nu_4$, $\nu_1 + \nu_5$). Right panel − the region of ν(CH) band of halothane.