

A cryosolution infrared and ab initio study of the van der Waals complexes of cyclopentene with hydrogen chloride and boron trifluoride

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Received 15 September 2004; accepted 21 October 2004

Dedicated to professor Dr. James R. Durig, mentor, colleague and friend, on the occasion of his 70th birthday.

Abstract

The formation of weak molecular complexes of cyclopentene with HCl and BF₃, dissolved in liquid argon is investigated using infrared spectroscopy. Evidence is found for the formation of 1:1 complexes in which the Lewis acid under study binds to the C=C double bond. At higher concentrations of HCl, weak absorption bands due to 1:2 species are also observed. From spectra recorded at different temperatures between 92 and 127 K, the complexation enthalpies for CP·HCl and CP·BF₃ are determined to be $-9.5(3)$ and $-16.1(9)$ kJ mol⁻¹, while for CP·(HCl)₂ a value of $-17.0(6)$ kJ mol⁻¹ is obtained. For the 1:1 and 1:2 complexes, structural and spectral information is obtained from ab initio calculations at the MP2/6-31+G(d) level. Using free energy perturbation Monte Carlo simulations to calculate the solvation enthalpies and statistical thermodynamics to account for zero-point vibrational and thermal contributions, the complexation energies for CP·HCl and CP·(HCl)₂ are estimated from the experimental complexation enthalpies to be $-17.4(14)$ and $-34.0(20)$ kJ mol⁻¹, while the value for CP·BF₃ was derived to be $-23.4(22)$ kJ mol⁻¹. The experimental complexation energies are compared with the theoretical values derived from the MP2/6-31+G(d) potential energy surfaces and with single point energies calculated at the MP2/6-311++G(3df,2pd) level.

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Keywords: van der Waals molecules; Hydrogen chloride; Boron trifluoride; Cryosolutions; Infrared spectroscopy

1. Introduction

Ever since the formation of complexes between ethene and hydrogen halides in argon matrices was first reported [1,2], van der Waals complexes of π -systems and pseudo- π -systems with typical Lewis acids such as, for example, hydrogen halides and boron halides, have been the subject of active experimental and theoretical research [3–21]. In most studies, the Lewis bases under investigation are limited to those in which the (pseudo-) π -system is part of a rigid structure in which no large amplitude motions occur.

To obtain information on the properties of complexes involving more flexible Lewis bases we have studied the

complexes of cyclopentene (CP) with hydrogen chloride, HCl, and boron trifluoride, BF₃, in liquid argon. The results of this study are reported below. It will be shown that for both Lewis acids, the formation of a 1:1 complex is observed, while for the solutions containing hydrogen chloride, evidence is also found for the presence of a higher complex, with 1:2 stoichiometry. For all complexes observed, experimental data on their vibrational spectra, their stoichiometry and their relative stability have been collected. In addition, theoretical data have been obtained from ab initio calculations at the MP2/6-31+G(d) and the MP2/6-311++G(3df,2pd) level.

2. Experimental

The samples of CP and BF₃ were purchased from Aldrich and Praxair, respectively, and were used without further purification. The HCl was synthesized in small

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amounts by hydrolyzing PCl_3 with water, and was purified by pumping the reaction mixture through a 180K slush, followed by fractionation on a low temperature, low pressure fractionation column. The argon used was supplied by Air Liquide and had a stated purity of 99.9999%.

The IR spectra were recorded on a Bruker IFS 66v Fourier transform spectrometer, using a Globar source in combination with a Ge/KBr beam splitter and a broadband MCT detector. The interferograms were averaged over 200 scans, Blackmann Harris apodized and Fourier transformed, using a zero filling factor of 4, to yield spectra at a resolution of 0.5 cm^{-1} . The experimental setup consists of a pressure manifold needed for filling and evacuating the cell and for monitoring the amount of gas used in a particular experiment, and the actual cell. The cell has a pathlength of 4 cm and is equipped with wedged Si windows.

3. Computational details

Ab initio calculations were performed using Gaussian03 [22]. During all calculations, corrections for BSSE were included explicitly by using CP-corrected gradient techniques [23].

Because of the relatively weak interactions between the monomers, the vibrations of the complexes can easily be subdivided into modes localized in the Lewis acid or Lewis base and into intermolecular van der Waals modes. The former can easily be correlated with the modes of the monomers, and we will describe them using the assignments of the monomer vibrations. To this end, the Herzberg numbering scheme of the monomers is used, and the symbol of the monomer is added as a superscript.

Solvation Gibbs energies of monomers and complexes were obtained from Monte Carlo perturbation calculations, using a modified version of BOSS 4.1 [24]. All simulations were run in the NPT ensemble, using periodic boundary conditions. The system consisted of one solute molecule surrounded by 256 solvent atoms. Preferential Metropolis sampling was used as described before [25]. An attempt to move the solute molecule was made on every 50th configuration and a change in volume was tried on every 600th configuration. The ranges for the attempted moves were the same in each calculation, and provided a $\sim 40\%$ acceptance probability for new configurations. The quantity calculated is the Gibbs energy $\Delta_{\text{sol}}G$ for the process of introducing one solute molecule into the box with solvent atoms via a coupling parameter λ . The path for $\lambda = 0$ (pure argon) to $\lambda = 1$ (a solution with one solute molecule) was completed in 50 equidistant steps. Each step consisted of an equilibrium phase for 20×10^6 configurations, followed by a production phase of 75×10^6 configurations. The Gibbs energy changes between the perturbed and reference systems were always small enough ($\approx kT$) to guarantee reliable results by the statistical perturbation theory.

For the monomers and the complexes, the Gibbs energies of solvation were calculated at 11 different temperatures

between 88 and 138 K, at a pressure of 28 bar. From these, the solvation entropies were determined using the expression $\Delta_{\text{sol}}S = -\partial(\Delta_{\text{sol}}G)/\partial T$, while the solvation enthalpies were obtained as $\Delta_{\text{sol}}H = \Delta_{\text{sol}}G + T\Delta_{\text{sol}}S$. The solute–solvent interactions were modelled using a set of atom–atom Lennard–Jones pair potentials to account for the dispersion and repulsion forces, and an additional term in which the polarization of the solvent atoms by the solute is accounted for using a first-order approximation [25,26]:

$$E_{\text{pol}} = -\frac{1}{2}\alpha(\vec{E} \cdot \vec{E})$$

in which α is the polarizability of the argon atoms and \vec{E} the electric field generated by the solute molecule.

4. Results

4.1. ab initio calculations

To gain insight into the structures and the relative stabilities of the complexes formed between CP and BF_3 and between CP and HCl, geometry optimizations were initiated starting from different relative positions of the molecules involved. For both HCl and BF_3 , the calculations converged to two minima, with C_s symmetry, in which the Lewis acid is situated on the *exo* or *endo* side of the CP moiety. The equilibrium geometries obtained for the complexes, and the structural parameters of interest, are shown in Figs. 1 and 2.

It should be noted here that in monomer CP a large amplitude motion is present due to the ring puckering mode, with a barrier separating the two minima of approximately $3\text{--}4 \text{ kJ mol}^{-1}$ [27,28]. In the complexes, this barrier separates the *exo* and the *endo* forms. The height of the barrier evidently can affect the characteristics of the

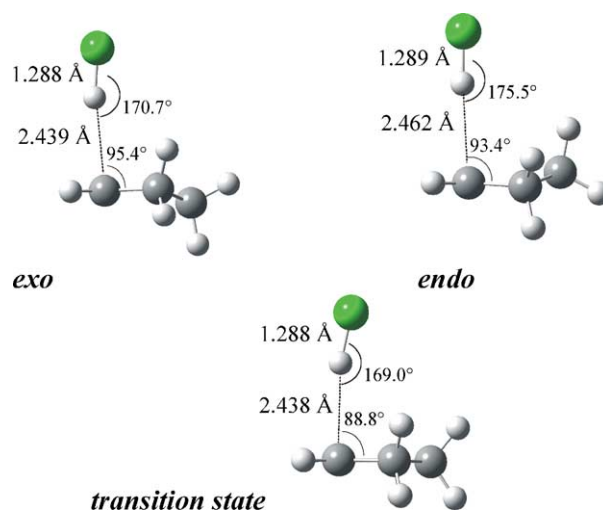


Fig. 1. MP2/6-31+G(d) equilibrium geometries and structural parameters for the *exo* and the *endo* conformation of cyclopentene-HCl. The conformers are shown looking down to the π bond. The transition state separating the two conformations, with a planar carbon-atom ring, is also shown.

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