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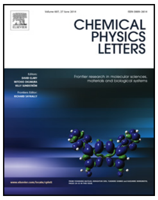

Editor's Choice

Infrared spectroscopic investigations of cationic ethanol, propanol, and butanol

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ABSTRACT

Infrared spectroscopy of the alcohol cations of ethanol, propanol, and butanol was performed to investigate their structures and hyperconjugation mechanisms. In the ethanol cation, the C—C bond hyperconjugates with the singly occupied molecular orbital (SOMO) at the oxygen atom, so that the C—C bond weakens and the bond length elongates. Multiple hyperconjugations among SOMO, the C—C bond, and the end C—H bond occur in the propanol cation and enhance the acidity of the C—H bond through the delocalization of its bonding σ electron. The butanol cation forms the oxonium-type structure through the proton transfer from the terminal CH bond.

1. Introduction

Reactions following proton transfer from CH bonds are often seen in ion-molecule reactions, ionization processes, and organic reactions involving partially-charged reaction intermediates such as carbocations, while neutral CH bonds have generally been regarded as aprotic [1–4]. These proton transfer processes imply enhancements of acidities of CH bonds in positively-charged states. Recently, several spectroscopic evidences for acidity enhancements of cationic CH bonds have been reported. The barrierless proton transfer reactions from the CH bond have been identified for the photo-ionized trimethylamine dimer through the structure analysis with the infrared (IR) spectroscopy [5]. The photoelectron spectrum of the dimethylether dimer has also implied the intracluster proton transfer from the CH bonds [6]. Furthermore, generations of protonated cations which should originate from proton transfer from CH bonds have frequently been observed in mass spectrometric investigations, so far [1,2,7,8]. For bare cations, low frequency shifts and intensity enhancements of cationic CH stretch bands have been reported for cationic toluene [9], propargyl radical [10], methanol [11], diethylether [12], tetrahydrofuran [13], and tetrahydropyran [13]. The spectral profiles of the latter three have been analyzed theoretically, and explained by the delocalization of bonding σ electrons of the CH bonds to the singly occupied molecular orbital (SOMO) through positive hyperconjugation [12,13]. The delocalization of the σ electrons weakens CH bond strengths and increases partial positive charge of the hydrogen atoms so as to enhance acidities of the CH bonds. All of these studies indicate that cationic CH bonds can act as proton sources with enhancements of donor abilities.

Alcohols are typical protic molecules because of the large polarization of the hydroxyl group. In the neutral state, their acidic site is the OH group and the acidity tends to decrease as a function of alkyl chain length because of the electron donating property of the alkyl group. The enhancements of the OH bond acidity of alcohol cations and protonated alcohols have undergone extensive investigations [14,15]. On the other hand, as mentioned above, the enhancement of the CH bond acidity in the methanol cation has also been implied by the IR spectroscopy [11]. Then, several questions arise for cationic alcohols. One is whether hyperconjugation mechanisms of alcohol cations are similar to those recently elucidated for the ether cations or not. The second is how long an alkyl chain can undergo enhancements of the CH acidity. Thirdly, can SOMO interact with CH bonds at the β and γ positions as well as those at the α positions?

To investigate these problems, in this study, we carried out IR spectroscopy for the ethanol, propanol, and butanol cations, which were generated by the vacuum ultraviolet (VUV) photoionization. Their structures, hyperconjugation mechanisms, and acidities of CH bonds were analyzed based on observed IR spectra and theoretical calculations of geometry optimization, harmonic vibrational simulations, natural bond orbital (NBO) analysis, and reaction path search.

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2. Experimental procedures and calculations

The IR spectroscopy of the alcohol cations was performed by IR predissociation spectroscopy of VUV-pumped ion (IRPDS-VUV-PI), of which details were described elsewhere [16]. Briefly, jet-cooled alcohol samples were ionized with the VUV photon at 118 nm. The produced ion was irradiated by the IR light ~20 ns after the VUV photoionization. IR spectra were observed by monitoring mass changes of the cation through vibrational predissociation following IR absorption by use of the time-of-flight (TOF) mass spectrometer. An IR enhancement spectrum was observed by monitoring the fragment ion (dehydrogenated alcohol cation) channel while an IR dip spectrum was observed by monitoring the parent ion channel. The enhancement spectrum showed essentially the same features as the dip spectrum for all the alcohol cations. Therefore, only enhancement spectra are shown in the main manuscript, while dip spectra are shown in the Supplementary material. The VUV light at 118 nm was generated by the third order nonlinear optical process through the Xe–Ar (1:10) mixture with the third harmonic (355 nm) of the Nd:YAG laser. The IR light was generated by the differential frequency generation of the second harmonic (532 nm) of the Nd:YAG laser and the dye laser output operated with the methanol solution of the DCM dye or the mixtures of the DCM and Rhodamine 640 dyes. The IR spectroscopy for the butanol cation was also performed by use of the tandem-type quadrupole mass spectrometer and the IR optical parametric oscillator (IR-OPO, LaserVision). In this setup, the butanol cation was mass-selected with the first mass filter and was irradiated by the IR light. The intensity of the dehydrogenated butanol ion arising from the IR predissociation was monitored through the second mass filter.

Geometry optimizations and harmonic vibrational calculations were carried out at the ωB97D-X/6-311++G(3df, 3pd) level with the GAUSSIAN 09 program package and simulated geometries are visualized with the MOLEKEL 4.0 program [17,18]. Simulated vibrational frequencies were scaled by 0.944. Reaction path search calculations were performed with the global reaction route mapping (GRRM) method [19–21]. To determine the scaling factor (0.944) for the simulated frequencies in the harmonic vibrational calculations, we compare the observed frequencies of the free OH stretches of the ethanol, propanol, and butanol cations and the hyperconjugated C_γH (C8-H12, see Supplementary material for the numbering of atoms) stretch of the propanol cation with their simulated frequencies in the most stable structures, and we take the best fit factor to these frequencies.

3. Results and discussion

Figure 1 shows (a) the observed IR spectrum of ethanol cation and (b and c) the simulated spectra of the stable structures depicted in the figure. These structures I and II are optimized at the ωB97X-D/6-311++G(3df, 3pd) level. In observed spectrum (a), the OH stretch band appears at 3457 cm^{-1} and the bands seen in the region from 2850 to 3150 cm^{-1} are assigned to CH stretches. The simulated spectrum of most stable structure I well reproduces these observed feature, while the simulated intense bands (C_αH stretches as discussed later) lower than 2600 cm^{-1} for structure II are not observed. Therefore, the spectral carrier of observed spectrum (a) is assigned to structure I. In the 118 nm photoionization of alcohol molecules, the nonbonding electron of the oxygen atom is ejected. In structure I, the $C_\alpha C_\beta$ bond distance is simulated at 1.75 Å while that in the neutral ground state is 1.51 Å [22]. The bond lengths and atomic charges of structures I and II are listed in the Supplementary material. This CC bond elongation is caused by the hyperconjugation between the σ orbital of the CC bond and SOMO of the oxygen atom. This type of hyperconjugation mechanism has recently been rationalized for the tetrahydropyran cation [13]. The simulated CC bond distance (1.75 Å) of structure I is much longer than that (1.59 Å) of the tetrahydropyran cation [13]. The ethanol cation is more flexible than the cyclic ether, so that the overlap of the two orbitals (the σ orbital of the CC bond and SOMO) can be more optimized. In structure II, two C_αH bonds next to the oxygen atom hyperconjugate with SOMO. This type of hyperconjugation has also been seen in the cations of methanol, diethylether, and tetrahydrofuran [11–13]. In this hyperconjugation, σ electrons of the C_αH bonds delocalize to SOMO, so that the C_αH bonds are weakened and the positive charges of their hydrogen atoms increase (details are seen in the Supplementary material). The antisymmetric and symmetric stretch frequencies of the hyperconjugated C_αH bonds in structure II are simulated at 2411 and 2563 cm^{-1}, respectively, with the large transition dipole moments. The difference in the hyperconjugation mechanisms of structures I and II originates from the orientation of the OH group with respect to the internal rotation about the CO bond. This is because the overlap manners of the orbitals with SOMO vary with the internal rotation of the OH group. Hence, the CC bond length and strength of the ethanol cation largely change with the internal rotation. Because of the large energy difference between the isomers, only structure I is observed under the present experimental condition. We have concluded the formation of structure II is minor based on the consistency of the IR spectroscopic and theoretical results, although there might remain the possibility that missing of structure II might be caused by the low IR predissociation efficiency in the low frequency region.

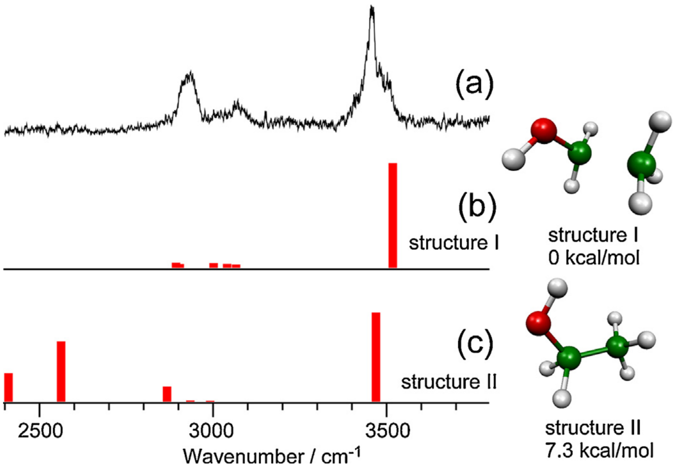

Figure 1. (a) Observed IR spectrum of the ethanol cation and (b, c) simulated spectra for the optimized structures at the ωB97X-D/6-311++G(3df, 3pd) level. The IR spectrum was observed by monitoring the dehydrogenated ethanol cation yield by use of the TOF mass spectrometer. Spectra (b) and (c) are simulated for structures I and II, respectively, depicted in the figure. Simulated vibrational frequencies in spectra (b) and (c) are scaled by 0.944.

Figure 2 represents (a) the observed IR spectrum of the propanol cation and (b and c) the simulated spectra of two types of stable structures, depicted in the figure. The other isomers and their simulated spectra are shown in the Supplementary material. All the isomers can be classified to the two types, which are represented by structures I and II in Figure 2, with respect to their hyperconjugation mechanisms. In observed spectrum (a), the band at 3525 cm^{-1} is assigned to the OH stretch vibration, of which single peak profile implies a single isomer dominantly exists. The other observed bands are assigned to the CH stretch vibrations. The simulated spectrum of structure I fits well with these observed spectral features. This indicates the propanol cation dominantly forms the structure I-type isomers. This is also supported by the simulated energy