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Double Proton Transfer-Induced Tautomerism of 4(3H)-Pyrimidinone Studied by IR Spectroscopy and Quantum Chemical Calculations

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Introduction. 4(3H)-pyrimidinone (4(3H)Pyr) (Figure 1.) has often been considered as a suitable model compound for studying the prototropic tautomerism of the nucleobases. A number of the combined experimental and theoretical studies have been performed for 4(3H)Pyr to predict its tautomeric stabilities and establish the vibrational assignments. However, the detailed information regarding the tautomerism and structure of 4(3H)Pyr in the solution phase is somewhat limited due in part to its poor solubility in less polar solvents. In the present study, we have investigated the tautomerism and structure of 4(3H)Pyr in the liquid solvent media: carbon tetrachloride (CCl_4) and chloroform ($CHCl_3$) solutions, using IR spectroscopy. Quantum chemical calculations were also employed to assist the interpretation of the experimental spectra and predict the relative stabilities of the 4(3H)Pyr species.

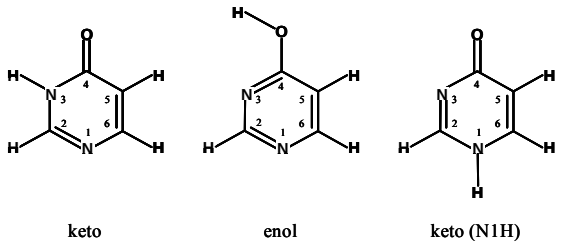

Fig 1 Three tautomeric forms: keto, enol, and keto (N1H), of 4(3H)Pyr.

Experiment. IR measurements were performed on a Nicolet 6700 FT-IR spectrometer at a spectral resolution of 1 cm^{-1}. 4(3H)Pyr/CCl_4 and 4(3H)Pyr/$CHCl_3$ solutions were prepared in concentration ranges of 0.01-0.5 mM and 0.2-10 mM, respectively. Concentration-dependent IR spectra of the freshly prepared samples were then recorded at room temperature. Temperature-dependent IR spectra were collected for the 4(3H)Pyr/CCl_4 solution over a temperature range of 20-60 ^oC in both heat-up and cool-down manners with an interval of 10 ^oC.

Calculation. Structural optimizations of 4(3H)Pyr were performed using the density functional theory (DFT) and *ab initio* MO methods at the Møller-Plesset second perturbation (MP2) level. The activation energy (E_a) of the keto ↔ enol tautomerization was estimated employing the QST2 method. All calculations were carried out using the Gaussian 03 program. The theoretical IR spectra were simulated assuming the Lorenzian band shape with 5 cm^{-1} full-width-at-half-height (FWHH).

Results and Discussion. Figure 2 shows the IR spectra in the NH and OH stretching (ν_{NH} and ν_{OH}) vibration regions observed during the heat-up process. At 20 ^oC, a band at 3395 cm^{-1} attributed to the ν_{NH} vibration of the keto monomer is clearly observed while that arises from the OH group of the enol monomer appears as a very weak absorption at 3540 cm^{-1}. As the temperature increases, both the ν_{NH} and ν_{OH} bands gradually increase in intensity, indicating the

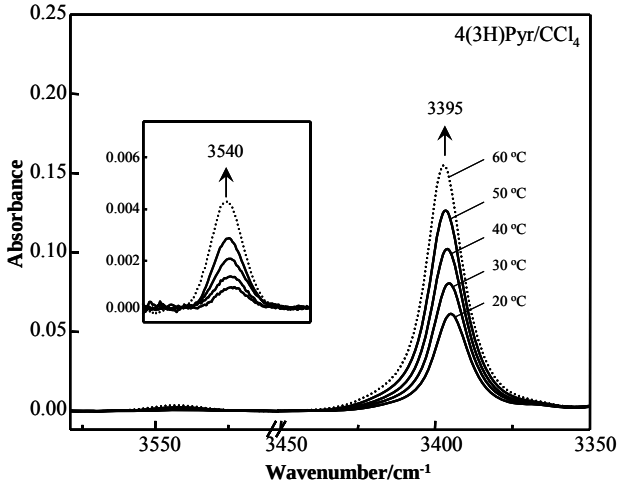

Fig 2 Temperature-dependent IR spectra of 4(3H)Pyr/CCl_4 in the NH and OH stretching vibration regions observed during the heat-up process.

increases in the populations of both the keto and enol monomers. The IR spectra observed during the cool-down process show a reverse spectral variation pattern. The intensities of the monomer ν_{NH} and ν_{OH} bands decrease while that of the dimer band increases during the course of temperature decrease.

Apparently, the increase in the population of the keto monomer is explainable by the dissociation of the KK ring dimer. The increase in the population of the enol monomer is of interest. It is improbable to consider the intramolecular keto ↔ enol tautomerization as the source of the increase in the population of the enol monomer. The origins of the enol monomer then fall into two possible mechanisms: 1) the dissociation of the KE ring dimer, which, as described previously, may exist in a minor amount in the solution and 2) the dissociation of the EE ring dimer transformed from the KK ring dimer via double proton transfer (DPT) reaction. The latter has been considered as being capable of introducing the DNA tautomeric transition without requiring the presence of the free rare tautomers. To check the energetic feature of this process, the energies of the TS species for the DPT reactions in the gas phase and CCl_4 solution were computed at the MP2/6-31G(d,p) level using the QST2 method followed by a vibrational analysis. The SCRF/PCM model was employed for the calculation of the solvation effect. Figure 3 illustrates schematic energy diagrams for the DPT reactions. The energy barriers of 8.78 and 7.52 kcal/mol were obtained for the gas phase and CCl_4 solution, respectively. These values are far lower than those for the PT reaction in the isolated monomer. The obtained calculation results indicate that the DPT reaction in the KK ring dimer is energetically accessible under the condition being investigated.

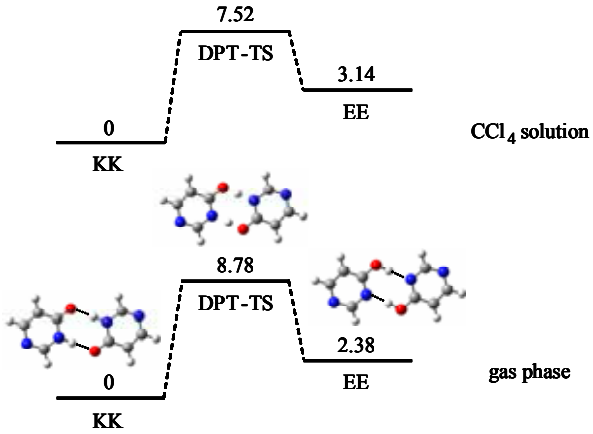

Fig 3 Schematic energy diagrams of the DPT reactions in the gas phase and CCl_4 solution.

As for the cool-down measurement, the enol monomer forms the EE ring dimer. However, the dimer thus formed tends to change to the most stable KK ring dimer via the DPT process. Consequently, the reverse IR spectral variation pattern is observed during the course of temperature decrease.