Direct Observation of Acid-Base Interaction by Means of Mass Spectrometry for Clusters

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(Received July 17, 1997; CL-970557)

The acid-base interaction could be visualized in the mass spectra of clusters isolated from solutions. The butyric acid-pyridine acid-base system in acetonitrile afforded clusters in which (butyric acid)$_1$(pyridine)$_1$ complex behaves like an unit species ; on the contrary, the butyric acid-pyrazine system afforded clusters in which butyric acid clusters, (butyric acid)$_n$, hold main structure. This clear difference is reasonably related with the relatively strong and weak acid-base interactions.

Acid-base interaction plays a vital role in various chemical reaction. This interaction in solution is mainly studied by IR and NMR methods in correlation with the pKa values,[1] and there are few studies on the basis of the microscopic structures at the molecular level.

It is reported herein that the acid-base interaction could be visualized by the mass spectrometric analysis of clusters isolated from solutions. Depending on the acid-base interaction, the resulting molecular clusters were found to be changed obviously. Butyric acid-pyridine and butyric acid-pyrazine systems showed good contrast in the clustering which reflects acid-base interaction.

The details on the mass spectrometry for clusters isolated

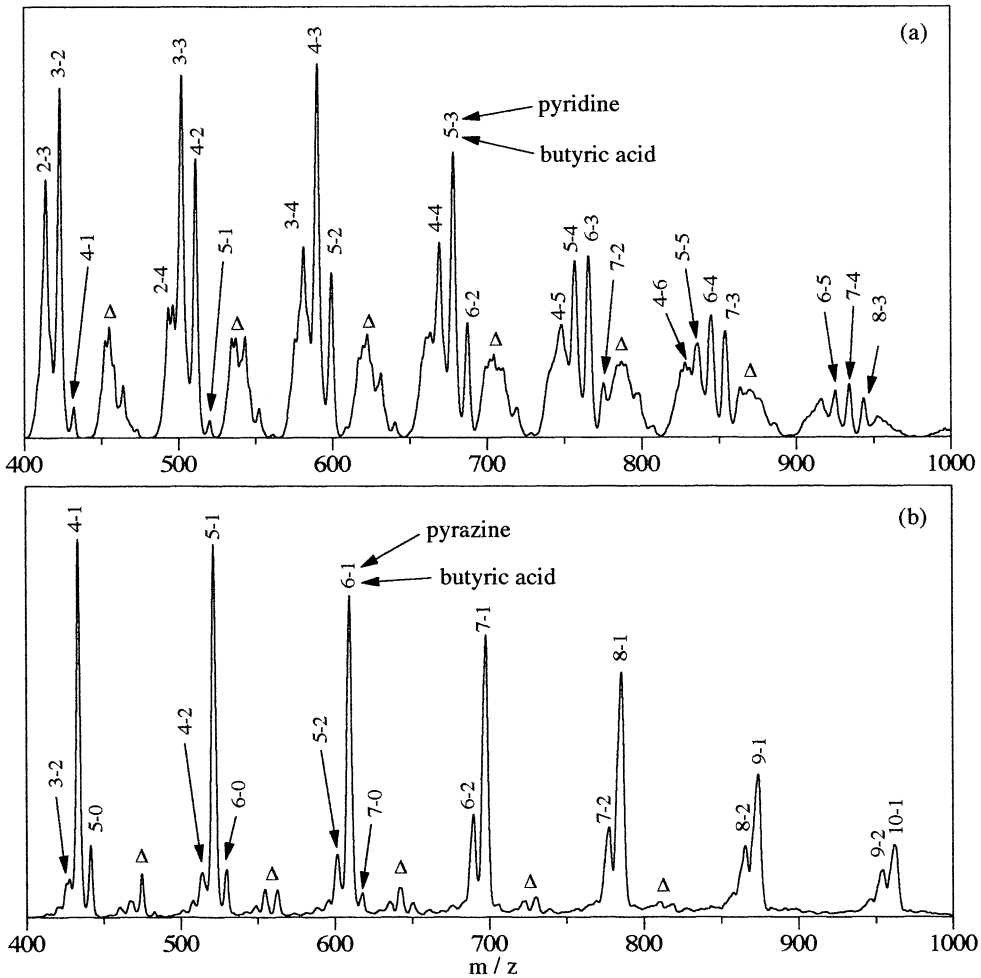

Figure 1. Mass spectra of clusters generated from solutions of (a) butyric acid / pyridine / acetonitrile with molar ratio 1:1:31 and (b) butyric acid / pyrazine / acetonitrile with molar ratio 1:1:31. The paired numbers represent (a) m-n for (butyric acid)$_m$(pyridine)$_n$ and (b) v-w for (butyric acid)$_v$(pyrazine)$_w$. The peaks marked by Δ are clusters solvated by acetonitrile. The nozzle temperatures are (a) 165 °C and (b) 210 °C.[4]

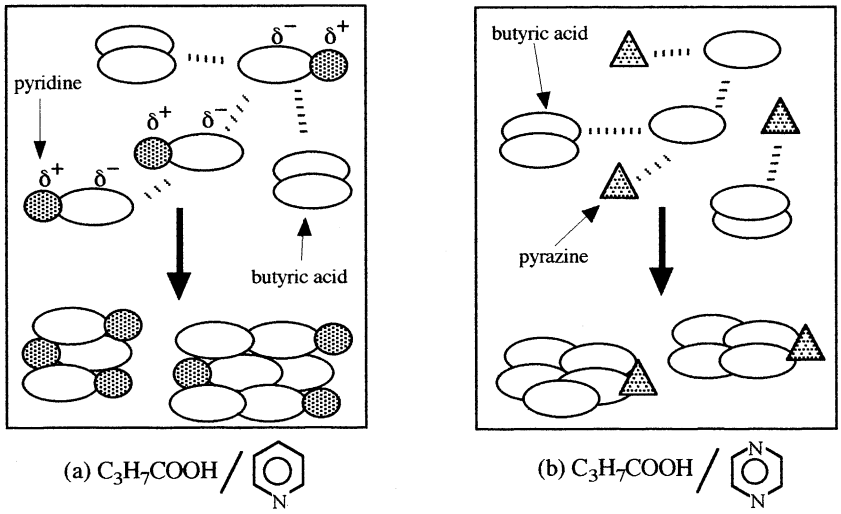

Figure 2. Schematic diagram of acid-base interactions for (a) relatively strong acid-base (butyric acid / pyridine system) and (b) relatively weak acid-base (butyric acid / pyrazine system). (a) Butyric acid and pyridine molecules form acid-base pairs, and acid-base clusters such as 3-3, 6-3, etc. are generated through the aggregation of these acid-base pairs in cooperation with the aggregation of butyric acid molecules themselves. (b) Since the acid-base interaction of butyric acid with pyrazine is weak, the inter-butyric acid interaction has an advantage over the formation of acid-base pair. Therefore, the resulting clusters are mainly composed of butyric acid molecules, such as 4-1, 5-1, etc.

from solution have already been reported previously.[2,3] The sample solution was injected into the vacuum chamber through a heated nozzle with a flow rate of 0.15 ml/min. Liquid droplets generated in the vacuum chamber were exploded by vacuum adiabatic expansion, which leads to the fragmentation of the liquid droplets into the clusters. The resulting clusters were analyzed by the quadrupole mass spectrometer after electron impact ionization with 30 eV. Each cluster was observed as a protonated species at this ionization energy. When much higher ionization energy was used, the larger clusters were difficult to be observed due to the disintegration by the excess energy.

Figure 1 (a) shows the mass spectrum of clusters generated from a solution of butyric acid / pyridine / acetonitrile (molar ratio : 1 / 1 / 31) mixture. The paired numbers in Figure 1 (a) represent m-n for $(CH_3(CH_2)_2COOH)_m(C_5H_5N)_n$. As prominent peaks m-n : 2-2, 3-2, 3-3, 4-3, 5-3, 6-3, 6-4, 7-4 etc. are observed. The smaller clusters are composed of equimolecular butyric acid and pyridine such as 2-2 and 3-3, and the relatively larger clusters include butyric acid molecules more than pyridine molecules such as 6-3 and 7-4. This indicates that the acid-base interaction between butyric acid and pyridine controls the formation of relatively smaller size clusters, and that the inter-butyric acid interaction becomes predominant with increasing the cluster size, which will be due to the steric effect. Therefore, the clusters have well-balanced molecular composition between the acid-base interaction and the steric effect.

On the other hand, Figure 1 (b) shows the mass spectrum for butyric acid / pyrazine / acetonitrile system (molar ratio : 1 / 1 / 31). The paired numbers written in Figure 1 (b) represent v-w for $(CH_3(CH_2)_2COOH)_v(C_4H_4N_2)_w$. The peaks v-w : 4-1, 5-1, 6-1, 7-1, 8-1, etc. are observed prominently. This indicates that the clustering among butyric acid molecules is more favorable than the interaction of butyric acid with pyrazine.

Since the basicity of pyrazine is much weaker than pyridine (pKa of the conjugated acid for pyridine : 5.2, pyrazine : 0.6), the acid-base interaction of butyric acid with pyrazine should be much weaker than that with pyridine. The molecular composition in the observed clusters in Figure 1 (a) and (b) is found to reflect this acid-base interaction obviously, as illustrated in Figure 2 schematically. As for the butyric acid-pyridine, relatively strong acid-base system, the acid-base pair will contribute to the clustering in competition with inter-butyric acid interaction. On the other hand, as for the butyric acid-pyrazine, relatively weak acid-base system, the inter-butyric acid interaction overwhelms acid-base interaction. Therefore, the difference in clustering reflecting acid-base interaction could be observed in the mass spectrometry.

Except for the acidity or basicity, the acid-base clustering was found to be controlled by the used solvent and the size of alkyl group of carboxylic acid. These will be reported in a full paper soon.

References and Notes

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4 The cluster structure is very sensitive to the nozzle temperature. At lower temperatures (around 130 °C), most clusters are solvated by acetonitrile, and their size are relatively small. At higher temperatures (around 180 °C) the solvated acetonitrile is vaporized and the aggregation of the acid and the base molecules are promoted to form relatively larger clusters.[2,3]