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Notes

Bamboo Salt Effects on Hydrolysis of Estertin(IV) Complex

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In Korea, bamboo salt has been sometimes ingested as supplementary health-food and remedy since it has been known to exhibit various therapeutic effects on inflammation, viral disease, diabetes, circulation disorders and cancer,[1-5] even though its effects are not completely understood. Actually, it has been used as additives for face cream, tooth paste, cosmetics, food additives, cleaning materials, and antibacteria.[6,7] Thus, both food and pharmaceutical scientists are interested in research of bamboo salt in order to illuminate its either therapeutics or effects. Bamboo salt has been known to contain various trace ions and to exhibit basic pH.[1] However, to date, its task-specific application to pure chemistry remains unexplored. On the other hand, the chemistry of 'estertin(IV) chlorides' has attracted considerable attention because of a PVC stabilizer with low mammalian toxicities[8-12] and interesting coordination chemistry since Akzo chemists discovered a convenient synthetic route.[13] Earlier systematic investigations on the estertin(IV) chlorides suggest that their chemistry and bonding modes are very sensitive to environment.[8,14,15] Thus, this paper reports a preliminary result on the bamboo salt effects on the hydrolysis of 3-methoxy-3-oxopropyltin(IV) trichloride, [$CH_3OOCCH_2CH_2SnCl_3$] that shows a penta-coordinated Sn(IV) geometry with the intramolecular carbonyl oxygen-to-tin coordination.[10]

According to inductively coupled plasma (ICP) analyses, Si (72.01 ppm), Al (15.57 ppm), and Fe (145.97 ppm) contents of bamboo salt increase significantly compared to those (Si = 0.50, Al = 1.84, and Fe = 1.84 ppm) of natural sodium chloride salt (Supporting Information), presumably coming from muds during the preparation of the bamboo salt. In contrast, sulfur contents (0.27 wt %) of the bamboo salt significantly decrease compared to the natural salt (0.39 wt %) by elemental analysis, presumably owing to formation and evaporation of SO_2. The XPS signal (168.38 eV) on the sulfur species of bamboo salt is very similar to that (168.4 eV) of $Na_2S_2O_3$ (Supporting Information).[16] The carbon contents (bamboo salt = 0.12 wt %; natural sodium chloride salt = 0.09 wt %) relatively increase. Aqueous solutions of reagent grade NaCl (Aldrich), natural salt (Taesung Food Inc.), and bamboo salt (Taesung Food Inc.) at room temperature are in the range of pH = 7.00-7.30, 8.20-8.40, and 10.00-10.90, respectively. In the case of bamboo salt, 2.65 wt % of the bamboo salt is insoluble in water. The insoluble precipitate was analyzed by SEM-EDX: magnesium species significantly increase (Supporting Information), presumably owing to formation of less water-soluble $Mg(OH)_2$ during the preparation of bamboo salt.

0.1 mmol (0.31 g) of [$CH_3OOCCH_2CH_2SnCl_3$] was dissolved in the 1.0 M aqueous solution (10 mL) of bamboo salt to take ^1H NMR spectra (Figure 1) for the hydrolysis effects of bamboo salt. At initial stage of the ^1H NMR, three groups of signals at 1.78 (triplet), 2.80 (triplet), and 3.75 (singlet) ppm were observed in the solution. The -OCH_3 (3.75 ppm) signal shows an upfield shift by 0.25 ppm compared to that (4.0 ppm) of the complex or the known carbonyl oxygen-to-tin coordinated complexes,[8,14,15] indicating that the carbonyl oxygen-to-tin coordination is dissociated in aqueous solution. Such a fact may be ascribed to the replacement of chlorides with aqua ligands in aqueous solution. The dissociation of chloride anions in aqueous solution was also confirmed by the reaction of [$CH_3OOCCH_2CH_2SnCl_3$] with $AgNO_3$ in water which promptly gives rise to the white precipitate of AgCl, indicating that the estertin(IV) complex produces [$CH_3OOCCH_2CH_2Sn(H_2O)_3$]$^{3+}$ species in water. The triplet chemical shifts at 1.78 and 2.80 ppm are unambiguously the signals of ethylene group. As the time goes, the ethylene signals decrease whereas another set of ethylene signals (1.69 and 2.60 ppm) are growing. Furthermore, the -OCH_3 signal decreases along with appearance of new signal at 3.42 ppm which is the resonance of CH_3OH in the solution. Finally, after 24 h, the original chemical shifts were replaced by new set of chemical shifts. Such facts can be explained by two steps hydrolysis of [$CH_3OOCCH_2CH_2SnCl_3$]. The first step is that [$CH_3OOCCH_2CH_2SnCl_3$] was fast hydrolyzed to [$CH_3OOCCH_2CH_2Sn(H_2O)_3$]$Cl_3$, and the second step is that [$CH_3OOCCH_2CH_2Sn(H_2O)_3$]$Cl_3$ was changed to [$HOOCCH_2CH_2Sn(H_2O)_3$]Cl_3 and CH_3OH. In contrast, the ^1H NMR of [$CH_3OOCCH_2CH_2SnCl_3$] in aqueous solution without bamboo salt showed a different pattern.

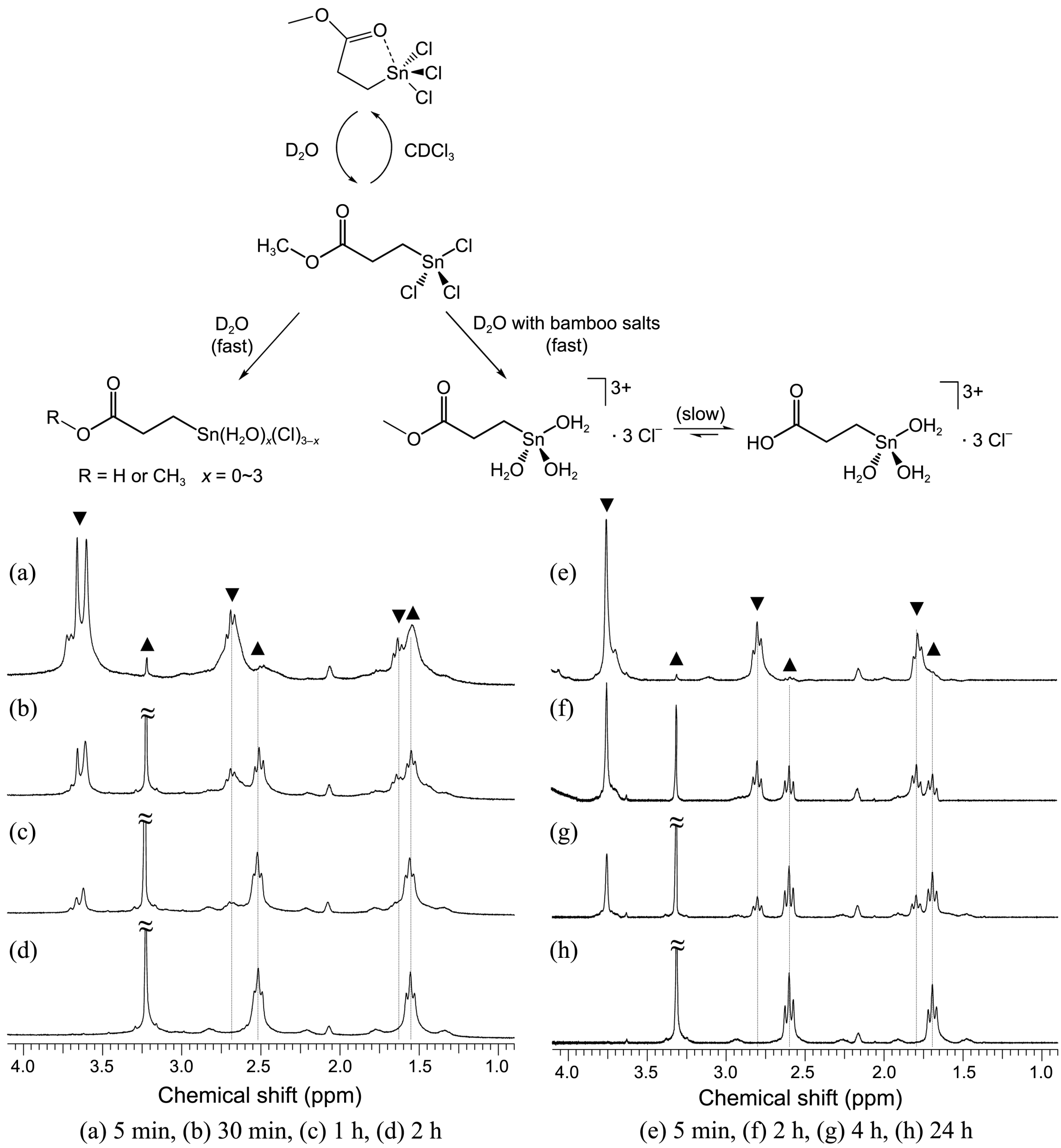

Figure 1. Schematic diagram of hydrolysis of [$CH_3OOCCH_2CH_2SnCl_3$] in D_2O (top) and ^1H NMR monitoring (bottom) in D_2O (a)-(d), and D_2O with bamboo salt (e)-(h).

First of all, the hydrolysis reaction is much faster as shown in Figure 1. The reaction was completed within 2 h in contrast to the long hydrolysis reaction time (24 h) with bamboo salts. Thus, for the fast hydrolysis reaction, the multi-signals of -OCH_3 moiety in the region of uncoordinated chemical shift (3.60 and 3.66 ppm) support that the mixture of [$ROOCCH_2CH_2Sn(H_2O)_{3-x}$]$Cl_x$ (R = CH_3, H; x = 0, 1, 2, and 3) exist at the initial stage. That is, the fast reaction could not clearly be separated into two steps. After the hydrolysis is completed, the final product for both reactions is convergent to the same [$HOOCCH_2CH_2Sn(H_2O)_3$]Cl_3. Such a result indicates that the bamboo salt retards the hydrolysis of 'estertin' into 'acidtin'. This retardation is also confirmed by the aqueous solution of simple sodium hydroxide instead of bamboo salt. Thus, the hydrolysis is very sensitive to pH in aqueous solution. According to Le Chatelier's principle, the first step with the bamboo salt should be slow. However, common ion effect of chloride in the first step seems to be not significant, because the first step reaction is very fast. The weak basic properties of bamboo salt are very useful to control or retard the sensitive hydrolysis reaction. The hydrolysis reaction is faster at high temperature, but sonication effect is not significant in the hydrolysis reaction. Formation of metal oxide *via* both 'alkaline' and 'salting out' of bamboo salt in aqueous solution is one of the interesting topics. Preliminary experiment discloses that the bamboo salts are very useful to formation of cobalt oxide (Supporting Information).

In conclusion, weak alkaline properties of bamboo salt are proved to be an effective task-specific retarder for the acidic hydrolysis on sensitive chemicals. This is the first application of bamboo salt to chemical reaction. Preliminary results support that the salt is useful to formation of metal oxide along with easy isolation. Further experiment on the components and reactions will contribute to the development of more detailed hydrolysis reaction.

Experimental

Typical Preparation of Bamboo Salts (Taesung Food Inc.). They are stuffed inside bamboo and covered with yellow mud, the products are then baked with pine wood and pine resin at about 1000 to 1500 °C for 8-10 h in a kiln, and then powdered. It is repeatedly stuffed inside the bamboo and baked. Finally, it is baked at about 1300 to 2000 °C.

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Supporting Information. ICP-AES analyses and XPS data of bamboo salt, SEM-EDX of water-insoluble powder of bamboo salt, and SEM image of cobalt oxide.

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