The Synthesis of Aluminium Hydroxide Distearate

An Infrared Spectroscopic Investigation

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Aluminium hydroxide disoap has been prepared by reacting isopropoxide disoap with water at room temperature and distilling off the resultant isopropanol at reduced pressure. The hydrolysis takes place with a preliminary step, where the water is connected to the carboxyl group of the soap by a hydrogen bond. Hydrolysis with heavy water gives evidence that the infrared absorption at 10.15 μm cannot be due to stretching vibrations of the AlO bond but must be referred to the bending vibrations of the OH groups.

Aluminium soaps and their synthesis have been investigated rather thoroughly since World War II. Their synthesis has usually been performed by one of three main methods. Reaction of potassium soap and aluminium salt in water solution gives a soap with a maximum of two stearic acid anions [1,2] and consequently trisoaps cannot be prepared in this way. In water-free systems the trisoaps have been synthesized from trimethylaluminium and fatty acid [3] and from aluminiumisopropoxide and fatty acid.[4,5]

The structure of the disoaps has been investigated by means of X-ray techniques [6-8] and infrared spectrometry. [8-10] The soaps both as solids (KBr-pellets) and as gels in hydrocarbons give absorptions as can be seen in Table 1.

Table 1. Infrared absorbance of aluminium disoaps after Bauer *et al.*[9] and Sheffer *et al.*[10]

μm	Group	Vibrations	Remarks
2.70	$-OH$	ν	Free hydrogen
6.1—6.4	COO^-	ν_a	—
10.15	$Al-O-Al$	—	—

The authors suggested that aluminium hydroxide disoaps were composed of aluminium-oxygen octahedra linked by the oxygen of the OH-groups and by the carboxyl groups bonded to two aluminium atoms (Fig. 1).
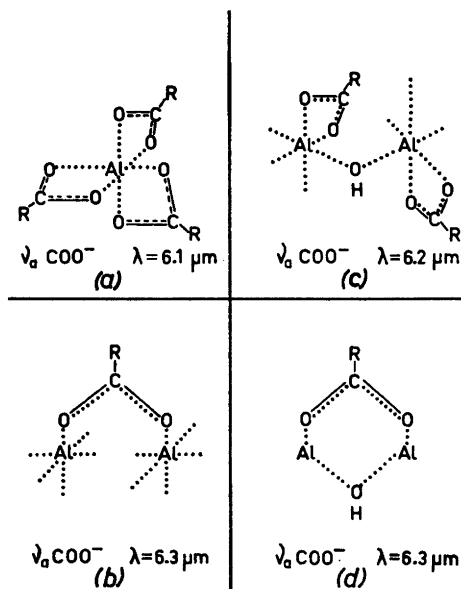
Fig. 1. Structure elements in aluminium soaps after Bauer [9] and Sheffer. [10] Trisoaps: (a) Mononuclear coordination; (b) Dinuclear coordination. Hydroxide disoaps: (c) Mononuclear coordination; (d) Dinuclear coordination.

The assignment of Al—O vibration to 10.15 μm was made by Bauer et al.[9] who could find no frequency shifts after substituting the OH-groups of the disoap with OD groups.

This investigation was performed in order to find a way of preparing aluminium hydroxide disoap of reproducible properties. The attempts to prepare the soaps by precipitating potassium soaps with an aluminium salt in water and extracting free stearic acid with dry acetone at 0°C have given soaps with poor reproducibility in their thermodynamic properties in the gelling process, in spite of the outmost care in their preparation. The hydroxide disoaps have now been prepared after slightly modified methods, which Mehrotra used for other disoaps.[11]

EXPERIMENTAL

Materials. The stearic acid (HSt) for the preparation was FLUKA A7380, which was used without further purification. The aluminium isopropoxide was KEBO purum, which was distilled (115°C/2 mm) in a nitrogen atmosphere immediately before use. The benzene was Merck p.a. which was dried with metallic sodium and carefully fractionated immediately before use. The water was plain distilled water without further purification and the heavy water was D_2O (99.7 %) from Norsk Hydro.

Preparation of the soap. 3 g $Al(OC_3H_7{}^i)_3$ was dissolved in 75 ml benzene and mixed with 8.358 g HSt in benzene. The isopropanol formed was distilled off under reduced pressure at a temperature that varied between 15 and 30°C. The lost C_6H_6 was compensated by an equal amount of dried C_6H_6 and the sample was divided into two parts. To one of those was added 0.0132 g H_2O and the isopropanol was distilled off as before after the reaction was finished. The second part was similarly treated with 0.0147 g D_2O. All operations were performed under a nitrogen atmosphere.

Determination of I.R.-spectra. The spectra were recorded by means of a Perkin-Elmer 221 spectrophotometer with a cell thickness of 0.102 mm. All spectra were compensated

for the solvent. The results are given as percent transmittance since overlapping bands and frequency shifts make absorbance a less attractive form of presenting them. Both cells were rinsed several times with dry C_6H_6 before use. All filling and cleaning operations were performed under a nitrogen atmosphere and the investigated substances were not exposed to the air during the investigation.

RESULTS

The I.R.-spectra of $Al(OC_3H_7{}^i)_3$ at two different concentrations can be seen in Fig. 2 together with two spectra of $C_3H_7OH^i$. The spectrum of $Al(OC_3H_7{}^i)_3$ coincides with that published by Goldenson et al.[12] except that the reported peak at $6.4-6.5$ μm is not to be found in the present spectrum and is consequently attributable to minor impurities. The abnormally high wave-length of CH stretching at 3.8 μm should be noticed in the spectrum of $Al(OC_3H_7{}^i)_3$.

The spectra of the solution at various times after the addition of stearic acid show no sign of unreacted acid after 1 min. The only time dependent changes after this are an increasing absorption around 6.1 μm and a slowly decreasing one at 6.3 μm. Fig. 3 shows the changes in the spectrum after the addition of the water to the solution of aluminium isopropoxide distearate. The hydroxide group shows absorption at 2.7 μm and the carboxyl group at 6.3 μm. The temporary absorption at 5.8 μm which disappears with time is remarkable. The absorption at 10.15 μm appears gradually at the same rate as the absorption at 2.70 μm. Fig. 4 shows the absorption when the isopropanol is distilled off. Fig. 5 shows the spectrum after the addition of deuterium oxide to the solution of alkoxide disoap, before and after removal of the alcohol, with the absorption at 10.15 μm changed to 13.0 μm.

DISCUSSION

The spectrum of $Al(OC_3H_7{}^i)_3$ in Fig. 2 shows an absorption at 3.8 μm. This must be due to one of the CH stretching modes, but has an unusually high wave-length. It seems probable that it has some connection with the bridging structure of the $OC_3H_7{}^i$-group and because of its weakness it is tempting to refer it to the tertiary hydrogen of the $OC_3H_7{}^i$-group of the bridges. The
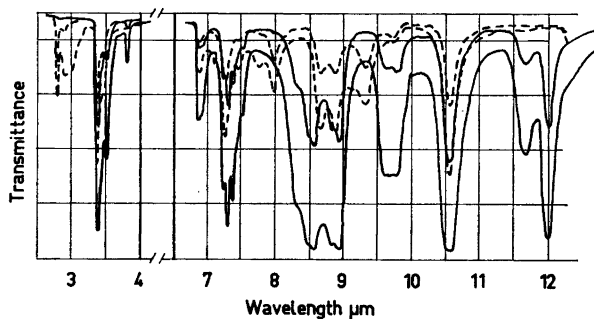

Fig. 2. Infrared spectra of $Al(OC_3H_7{}^i)_3$ ——— and $C_3H_7OH^i$ ---------- in benzene solution.

splitting of the absorption between $7-8$ μm and around 12 μm is also due to differences between $OC_3H_7{}^i$-groups in the bridges and at the terminal position.

In the reaction between one mole $Al(OC_3H_7{}^i)_3$ and two moles stearic acid, the acid is consumed in less time than is needed to record the spectrum around 6 μm, which means less than one minute. The carboxyl group absorbs mainly at 6.33 μm, but it has also a minor peak at lower wave-length about $6.1-6.2$ μm. The last-named absorption decreases to a marked degree, when the alcohol is distilled off and reappears when alcohol is added. This absorption is evidently due to interaction between the carboxyl groups of the soap and the alcohol molecules. This interaction contains a hydrogen bond of the OH-group of the alcohol which is proved by the ratio between the absorption of hydrogen bonded OH and free, which is larger in the present spectrum than in the spectrum of isopropanol in benzene of the same concentration at Fig. 2. A hydrogen bond from the alcohol would disturb the symmetry of the electron distribution in the carboxyl group and cause the decrease in the wave-length of the infrared absorption.[13]

When water is added to the solution, the hydroxide group of the disoap (2.70 μm) and of the isopropanol $(2.8-3.0$ $\mu m)$ appear at the same rate. The absorption at 10.15 μm, earlier believed to be $Al-O$ vibrations, can also be seen at Fig. 3. The increasing absorption at 5.85 μm which gradually disappears

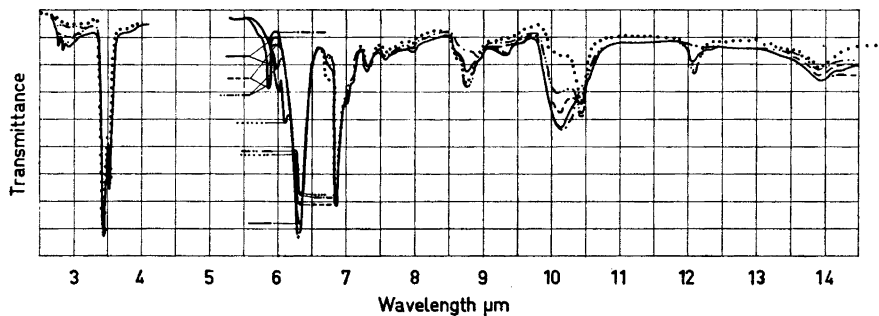*Fig. 3.* Infrared spectra of a solution of aluminium isopropoxide distearate after addition of water. ... Before addition, ------ 10 min, ----------- 1 h, ——— 6 h, and --.--.-- 20 h after addition.

again before the reaction is completed, is interesting. It could be explained by assuming the formation of free acid which again reacts with an intermediate aluminium-compound, but the following proposal seems more reasonable.

The preliminary step in the reaction is connection of the hydrogen atoms of a water molecule to the carboxyl group of the soap *and* to the isopropoxide as in Fig. 6. The hydrogen bonds give a shift in the electron distribution in the carboxyl group of the soap which causes the group to absorb at a shorter wave-length, around 5.8 μm. The hydrogen bond between water and the isopropoxide group displaces the electron pair between aluminium and the oxygen of the alcohol towards the latter. This means an increase of the positive charge of the aluminium atom which makes the connection of the water oxygen to aluminium and the removing of the alcohol molecule easier.

The reaction is possible since the substitution of the isopropoxide group with the hydroxide group gives an energetically more favourable structure around the aluminium atom. This is evident from the fact that the isopropanol formed has no influence on the carboxyl group absorption, which is at 6.33 μm in this case.

When the alcohol is removed by careful distillation at reduced pressure there is no change in the carboxyl absorption at 6.33 μm which shows that the alcohol has no connection to the group (Fig. 4). It is interesting to note that
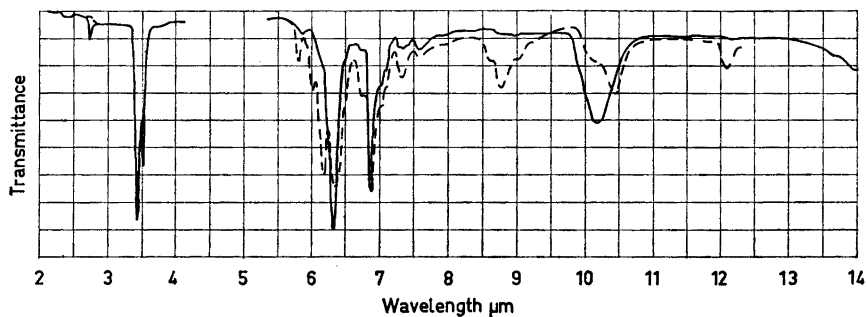

Fig. 4. Infrared spectra of aluminium hydroxide distearate in benzene. — — — C_3H_7OH removed by distillation at atmospheric pressure and 80°C, ———— at room temperature, reduced pressure.

the absorption of the OH-groups of the hydroxide disoaps has a shorter wavelength than the absorption of OH-groups of the alcohol which are not hydrogen bonded. An attempt to distill off the alcohol at atmospheric pressure led to decomposition. This will be investigated in detail later. The soap shows also the absorption at 10.15 μm which earlier was believed to be due to AlO-bonding of the hydroxide group. In order to confirm this the alkoxide disoap was hydrolyzed with deuterium oxide. The results were quite analogous to those obtained with water, of course with the changes expected from the substitution of H by
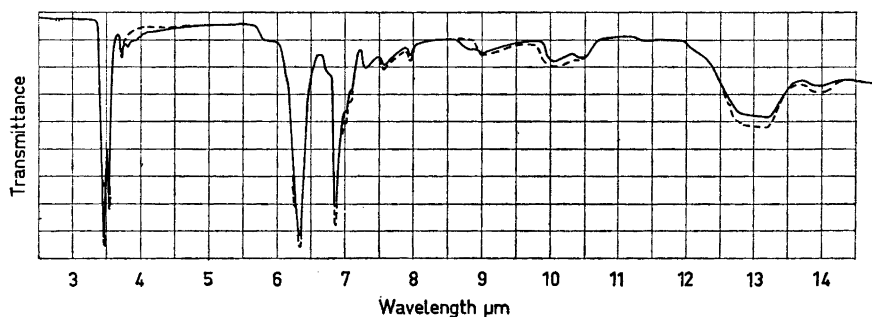

Fig. 5. Infrared spectra of aluminium isopropoxide distearate in benzene after addition of deuterooxide, ———— before, — — — after removal of C_3H_7OD.

D. The supposed absorption of AlO bond did not, however, appear at 10.15 μm (Fig. 5). Instead the spectrum contained an absorption at 13.0 μm which was not removed, when the alcohol was distilled off. This result gives clear evidence that the absorption at 10.15 μm of the hydroxide disoap cannot entirely be due to AlO vibrations. It seems reasonable to refer it to a bending mode of the OH-group with some degree of coupling to the AlO stretching vibration, since the frequency ratio is 1.29, instead of the theoretical value of 1.37 for a harmonic oscillation. Such a coupling seems quite natural since the OH bending vibrations are commonly coupled to CO stretching vibrations in alcohols, carboxylic acids, *etc.*

Conclusion. The synthesis of aluminium hydroxide distearate was achieved by reacting isopropoxide distearate with water at room temperature and distilling off the resultant isopropanol at reduced pressure.
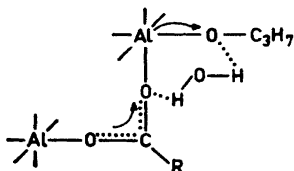

Fig. 6. Preliminary step in the reaction between water and aluminium isopropoxide disoap.

The increased stability of the coordination bonds to the aluminium ion when the isopropoxide group is replaced by the hydroxide group is evident from the fact that isopropanol formed when isopropoxide distearate is prepared has a pronounced effect on the frequency of the infrared absorption of the carboxyl group. The isopropanol formed when the isopropoxide is replaced by hydroxide has no influence on the carboxyl absorption at all.

Comparison between spectra of aluminium hydroxide distearate and aluminium deuteroxide distearate has given evidence that the infrared absorption at 10.15 μm cannot be due to the stretching vibration of the AlO bond. The shift of frequency when substituting hydrogen by deuterium indicates that the absorption arises from bending vibrations of the OH-group, possibly with some coupling to an AlO stretching vibration. The work will continue with the investigation of aluminium soaps of different composition.

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