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Reaction of Iron(III)-Form Ion Exchanger with Acetylacetone

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It was found that ferric ions are removed from resin by acetylacetone(Hacac) to form trisacetylacetonatoiron(III), Fe(acac)$_3$. By the addition of a small amount of pyridine-water mixture to the iron(III)-form resin in acetylacetone milieu, the ferric ions are quantitatively removed from the resin, and in their place the pyridinium ions are adsorbed onto it. The reaction was successfully applied to the synthesis of Fe(acac)$_3$ in over 95% yield.

The conversion of a metallic ion on the cation exchanger into a chelate compound based on the ion exchange reaction in organic medium was investigated.

It was anticipated that if the resin suspended in an organic solvent is brought in contact with a chelating reagent such as β-diketone, the metal ions on the resin will be pulled out into the solvent in the form of metal chelate and the protons liberated from the β-diketone are adsorbed on the resin in place of the metal ions, as shown by

$$(RSO_3)_3Fe + 3Hacac = 3RSO_3H + Fe(acac)_3 \quad (1)$$

where R denotes the resin matrix.

In this paper the reaction of iron(III)-form Amberlyst 15 with acetylacetone is described.

Experimental

Apparatus and Reagents. Absorption measurements were carried out on a Shimadzu QV-50 spectrophotometer and a Hitachi 356 two-wavelength double-beam spectrophotometer with 10 mm cells. A Hitachi 063 type gas chromatograph with a thermal conductivity detector was used. Acetylacetone and pyridine (analytical grade, Wako Pure Chemical Inc.) were used without further purification.

Preparation of Iron(III)-Form Resin. The sulfonic acid cation exchanger, Amberlyst 15,[1] with a macroreticular structure was used, Commercial Amberlyst 15 was crushed and sieved to a fraction of 60—80 mesh. The resin was first washed with ethyl alcohol to remove impregnated toluene, and then with water, and treated with 4 M hydrochloric acid. The water-washed hydrogenform resin was treated with 0.1 M ferric nitrate. The resulting iron(III)-form resin is washed with water until the washings showed no color reaction with potassium ferrocyanide,[2] air dried, and then stored in a desiccator.

A part of ferric ion on the resin might be expected to coordinate hydroxyl ion, *e.g.*, (RSO$_3$)$_2$FeOH. In this case, the corresponding ion exchange reaction would proceed as follows,

$$(RSO_3)_2FeOH + 3Hacac = 2RSO_3H + Fe(acac)_3 + H_2O \quad (2)$$

Determination of Ferric Ions on the Iron(III)-Form Resin. The ferric ions on the 100 mg portion of the dried iron(III)-form resin were eluted with 2 M hydrochloric acid and determined spectrophotometrically with *o*-phenanthroline method. It was found that the 4.52±0.10 meq of ferric ions are adsorbed per 1 g of the dried iron(III)-form resin.

Conversion of Ferric Ion on the Resin into Acetylacetonate. A test tube containing 5 mg of dried iron(III)-form resin and 3 ml of acetylacetone was dipped into the water bath kept at 70±1 °C and shaken by hand for 5 min. A pyridine-water mixture was then added and warmed again for 5 min. After filtration, the resin was washed with ethyl alcohol and then with water. The ferric ions remaining on the resin were eluted by 2 M hydrochloric acid, and determined spectrophotometrically by the *o*-phenanthroline method.

Results and Discussion

Reaction of Ferric-Form Resin with Acetylacetone. In the course of the reaction, the color of the solution turned red as a result of the formation of tris(acetylacetonato)iron(III) complex identified by spectrophotometry. It was found that although the reaction shown by Eqs. (1) and/or (2) occurs, a considerable amount of iron is firmly retained on the resin. The phenomenon has not bee clarified.

Effect of Pyridine and Water. Conditions were studied for the complete liberation of iron from the resin. Addition of a pyridine-water mixture was found to be highly effective (Figs. 1 and 2). Addition of an appropriate amount of pyridine or water was effective to some extent, but a mixture of the two was the most effective, more than 99% of iron ions being removed from the resin by addition of the 2:1 to 1:5 pyridine-water mixture, 5—7% of the volume of acetylacetone employed. In the presence of the pyridine-water mixture, the dissociation of Hacac takes place as follows.

$$py + H_2O = pyH^+ + OH^-$$
$$Hacac + OH^- = acac^- + H_2O$$

The resulting acetylacetonate anion attacks the ferric

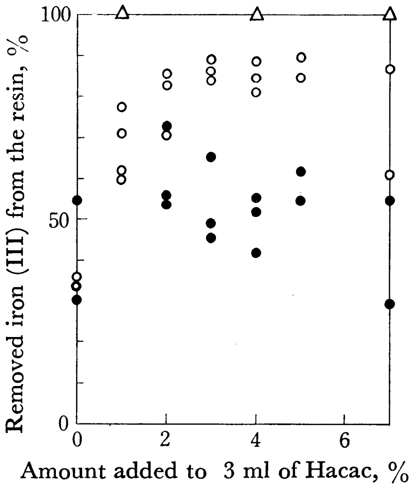

Fig. 1. Effect of the addition of pyridine (●), H$_2$O (○), and their 1:2 mixture (△) on the removal of the iron(III) from the 5 mg of the resin with 3 ml of Hacac.

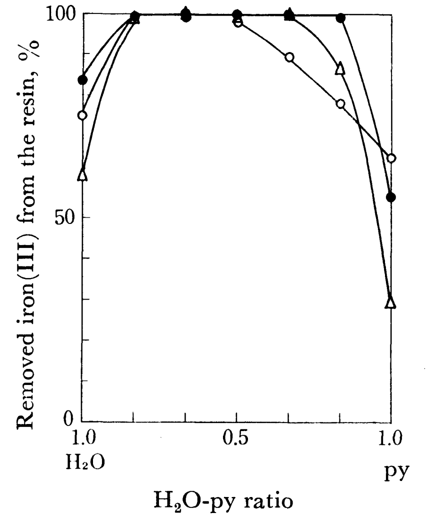

Fig. 2. Effect of the pyridine-water mixture with various ratio on the removal of the iron(III) from the 5 mg of the resin with 3 ml of Hacac. The ratio of the pyridine-water mixture added to Hacac is 1% (○), 5% (●), 7% (△) in Hacac, respectively.

ion on the resin, while the pyridinium ion competes with the ferric ion for the site, namely, the former withdraws the ferric ion from the resin and the latter is adsorbed on the resin in place of the ferric ion. One reaction predicted is shown by

$$(RSO_3)_3Fe + 3Hacac + 3py \xrightarrow{H_2O} 3RSO_3Hpy + Fe(acac)_3 \quad (3)$$

It was necessary to analyze the $Fe(acac)_3$ in the resulting solution and to detect the pyridinium ion on the resin.

Absorption Spectra of the Resulting Solution. After completion of the above procedure, the resin was filtered and washed with acetylacetone, all the washings being collected into a 20 ml volumetric flask, and then a 5 ml portion of the solution was taken out and the flask was filled up to 10 ml with Hacac. A comparison of the absorption spectra of the solution and that of synthesized one in which the corresponding amount of $Fe(acac)_3$ is dissolved in Hacac is shown in Fig. 3. The synthesis of $Fe(acac)_3$ is described later. It may be said that the compound is formed quantitatively by the reaction of iron(III)-form resin with Hacac.

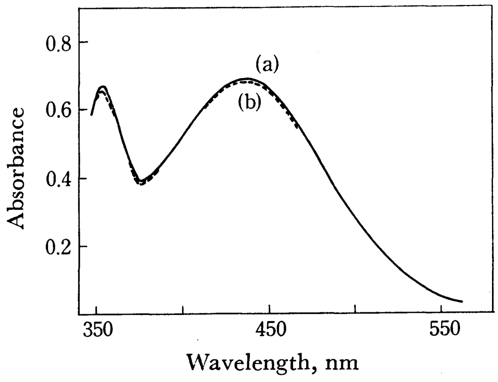

Fig. 3. Comparison of absorption spectra of $Fe(acac)_3$ in Hacac. (a) Synthesized chelate, 1.888×10^{-4} M, (b) Solution obtained by present method *vs.* Hacac.

Test for Pyridinium Ion on the Resin. The resin separated by filtration was further washed with ethyl alcohol and then with water until the washings gave no pyridine odor. A small amount of the 1 M sodium hydroxide was poured onto the resulting resin to elute the presumed pyridinium ion on the resin. The eluate having a strong pyridine odor was analyzed by gas chromatograph on the 1 m column packed with 30% PEG 4000 on 80—100 mesh Chromosorb W, at 90 °C. A pyridine peak appeared on the chromatogram indicating that the pyridinium ion had been adsorbed on the resin. The desorption of iron might proceed according to scheme (3). The sequence of addition of reagents is important, because if pyridine and water are present at the beginning of the reaction, they are adsorbed onto the metal ions on the resin and hinder the contact of Hacac with metal ions as confirmed experimentally.

Application to the Synthesis of the Chelate Compound. Treat 500 mg of iron(III)-form resin with 10 ml of Hacac and then add 0.5 ml of pyridine-water (1: 2) solution. After the reaction, separate the resin by filtration and wash it with a small amount of Hacac, and collect the filtrate into a test tube. Heat to 130 °C and boil off the excess Hacac and pyridine by bubbling nitrogen gas. Collect the crude $Fe(acac)_3$ at the bottom of the test tube, and press it with glass wool. Narrow the neck of the test tube, and put it into a vessel connected to a vacuum pump, by heating the bottom of the tube to 190 °C at 1 Torr. The chelate deposits at the neck of the test tube. The mp of the chelate 181—183 °C (reported,[3] 181.3—182.3 °C); results of elemental analysis: Found: C, 50.98; H, 5.94%. Calcd for $Fe(C_5H_7O_2)_3$: C, 51.01; H, 5.99%. The yield of duplicate synthesis was 96 and 97%, respectively.

The reaction may commonly occur between the metallic form ion exchanger and chelating agent. Recently Higgins[4] applied the method to the preparation of cesium lanthanoid hexafluoroacetylacetonates. A reaction of this kind might have a wide applicability.

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