The Comparison of Zirconium Tetrachloride with Aluminum Chloride as a Friedel–Crafts Catalyst

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The recent availability of zirconium tetrachloride in commercial quantities has prompted the investigation of this material as a catalyst for the synthesis of ketones according to Friedel and Crafts. Krishnamurti has previously reported[2] zirconium tetrachloride to be effective in the preparation of the ketones acetophenone and benzophenone.

We have conducted a preliminary comparison of zirconium tetrachloride with aluminum chloride by measuring the yields of *p*-methyl-acetophenone from acetyl chloride and toluene. The procedure and analytical method used in this investigation were essentially those developed by Dermer and co-workers.[3,4]

The yields of ketone obtained with zirconium tetrachloride and aluminum chloride are set forth in the accompanying graph. It will be seen that the results with zirconium tetrachloride are at once better but less consistent than those obtained with aluminum chloride. No explanation is offered for the erratic behavior of zirconium tetrachloride.

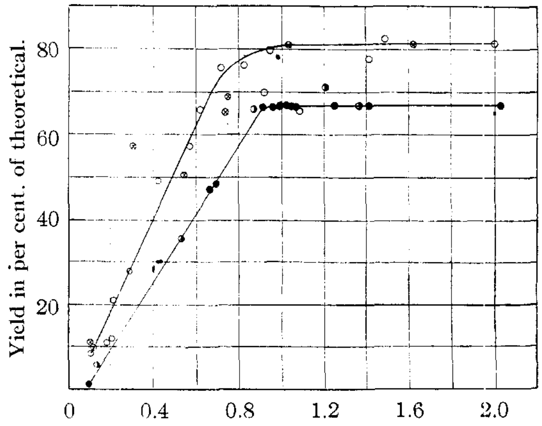

Fig. 1—Variation of yield of *p*-methylacetophenone with mole ratio of catalyst/acetyl chloride: ●, $AlCl_3$ at 100°; ◑, $AlCl_3$ at room temp.; ○, $ZrCl_4$ at 100°; ⊕, $ZrCl_4$ at room temp.

Macro runs in which the *p*-methylacetophenone was actually isolated and weighed gave essentially the yields predicted by the semi-micro method of Dermer. In these macro runs very efficient stirring was found necessary; no stirring was used in the micro runs.

The investigation is being continued.

Experimental

Reagents.—Eastman Kodak Co. toluene and Merck acetyl chloride were used.

Zirconium tetrachloride was obtained from the Titanium Alloy Manufacturing Company and anhydrous sublimed technical aluminum chloride was purchased from Eimer and Amend. All of the above reagents were used without further purification.

Procedure.—The modifications to the original procedure of Dermer adopted by Dermer and Billmeier[4] were used in this investigation. The time of reaction for all experiments heated at 100° was one hour. For all experiments carried out at room temperature, the time of reaction was two hours.

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[3] O. C. Dermer, David M. Wilson, F. M. Johnson and V. H. Dermer, This Journal, **63**, 2881 (1941).

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Sodium Hydrogen Citrates

By David I. Hitchcock

Primary and secondary sodium citrates were described long ago by Heldt[1] and by Salzer,[2] but their analytical data are hardly adequate to prove that the salts were pure substances. No recent account of the preparation and analysis of acid sodium citrates has been found, and they are not listed in available catalogs of pure chemicals. Because of the possible use of these salts for the preparation of buffers and for the preservation of blood,[3] it seemed worth while to re-investigate their preparation and composition.

It was found that microscopic crystals of either salt could be obtained from aqueous solutions containing approximately the calculated proportions of acid and alkali, but that the crystals did not have the theoretical ratios of sodium to acid hydrogen unless the composition of the solutions was very carefully controlled. Preparations which contained a 1 to 4% excess of acid or base could be purified by one or two recrystallizations from water.

Pure salts were obtained without recrystallization by preparing the solutions from anhydrous citric acid, dried at 70°, and anhydrous sodium carbonate, dried at 160°. One-mole portions of the acid were dissolved in 600 ml. of water, and the calculated amounts of carbonate were added in small portions, with stirring. The solutions were boiled for half an hour, filtered into weighed evaporating dishes, and concentrated on a steam-bath until the remaining water weighed 75 to 85% as much as the dry salt. Cooling to 20 or 10° yielded pastes of microscopic crystals; the disodium salt had the form of square needles or rectangular prisms, while the crystals of the monosodium salt appeared to be nearly perfect cubes. After filtration with suction, small filtrates containing about 25% of the materials were discarded. The crystals were air-dried, ground to pass a 20-mesh sieve, and dried at 70°.

Acid hydrogen was determined by titration with 0.1 *M* sodium hydroxide, free from carbonate, standardized against potassium hydrogen phthalate. The end-point chosen for the titrations was *p*H 9.2, as estimated by means of phenolphthalein indicator and a comparison solution of pure borax. Sodium was determined by conversion to the sulfate. Because of the large amounts of gas evolved in the decomposition of citrates by sulfuric acid, it was necessary to increase the temperature very gradu-

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