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

BY H. W. HEINE,[1] D. L. COTTLE AND H. L. VAN MATER

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.

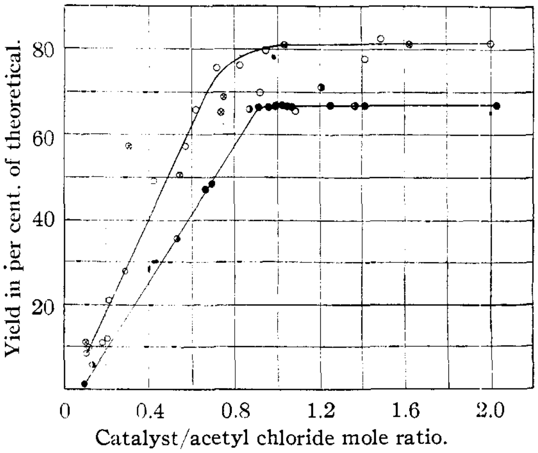

Fig. 1—Variation of yield of *p*-methylacetophenone with mole ratio of catalyst/acetyl chloride: ●, $AlCl_3$ at 100°; ◑, $AlCl_3$ at room temp.; ○, $ZrCl_4$ at 100°; ⊕, $ZrCl_4$ at room temp.

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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[2] P. Krishnamurti, *J. Madras Agr. Students Union*, **40** (1928).

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

[4] O. C. Dermer and Robert Billmeier, *ibid.*, **64**, 464 (1942).

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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[1] W. Heldt, *Ann.*, **47**, 157 (1843).

[2] Th. Salzer, *Arch. Pharm.*, **229**, 547 (1891); **231**, 514 (1893).

[3] J. F. Loutit and P. L. Mollison, *Brit. Med. J.*, **1943**, II, 744.

ally; periods of a day or night at 110, 320 and 540° were adequate when followed by ten-minute heatings to constant weight at about 800°. These analyses showed that the ratio of sodium to acid hydrogen was 0.500 ± 0.001 for the monosodium salt, and 2.002 ± 0.001 for the disodium salt. The analyses also indicated a formula weight of 215.4 for the monosodium salt and 263.5 for the disodium salt. The former figure is somewhat more than 214.1, the formula weight of anhydrous monosodium citrate, while the latter figure indicates that the disodium salt contained 1.5 moles of water, which would make the calculated value 263.1. The air-dried preparations of both salts lost less than 0.5% in weight at 70 or 110°, and also remained constant in weight when kept over a saturated sodium chloride solution at room temperature. The monosodium salt became caked on standing in a stoppered bottle, but titration of the caked material did not reveal any absorption of moisture. The disodium salt could be dried more rapidly after washing with 95% alcohol, which did not remove the 1.5 moles of water. Alcohol withdrew a little acid from the monosodium salt. None of the preparations of either salt had the composition of the monohydrates reported by Heldt[1] and Salzer.[2]

These acid citrates differ from many other acid salts, such as the phosphates, in one important respect. Either of the acid citrates by itself forms a well buffered solution in water. The following *p*H values were obtained for 0.1 and 0.01 *M* solutions at 25°: monosodium citrate, 3.70 and 3.88; disodium citrate, 4.96 and 5.30, respectively. These values, which were checked within 0.003 *p*H with solutions made from three different preparations of each salt, were obtained by means of a carefully tested glass electrode in a water-jacketed cell with liquid junction, similar to that described in a previous paper.[4] They are based on a *p*H value of 4.008 for 0.05 *M* potassium acid phthalate.

Reliable solutions may also be obtained, without isolating the acid salts, from carefully standardized solutions of citric acid and sodium hydroxide, according to Sörensen.[5]

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[4] D. I. Hitchcock and A. C. Taylor, This Journal, **59**, 1812 (1937).

[5] S. P. L. Sörensen, *Biochem. Z.*, **21**, 131 (1909).

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Studies on the Willgerodt Reaction. I. Some Extensions of the Reaction

BY JOHN A. KING AND FREEMAN H. MCMILLAN

Nearly sixty years ago Willgerodt[1,2] discovered the reaction which has come to bear his name: treatment of an aliphatic aromatic ketone with yellow ammonium sulfide at a moderately high temperature in a sealed tube to effect the transformation of the ketone to an aralkyl amide. Until Cavalieri, Pattison and Carmack[3] announced, last October, their application of the reaction to purely aliphatic and to alicyclic–aliphatic ketones, the assumption had always been implied that the reaction was confined to aromatic–aliphatic ketones. We have likewise found that this assumed restriction does not exist.

$$C_6H_5COCH_3 \xrightarrow{(NH_4)_2S_x} C_6H_5CH_2CONH_2$$

When phenylacetone was treated with yellow ammonium sulfide under the same conditions as used by Willgerodt and Merk[4] for propiophenone the product was β-phenylpropionamide.

$$\begin{aligned} &C_6H_5CH_2COCH_3 \xrightarrow{(NH_4)_2S_x} \\ &\qquad C_6H_5CH_2CH_2CONH_2 \xleftarrow{(NH_4)_2S_x} C_6H_5COCH_2CH_3 \end{aligned}$$

After it was thus shown that the carbonyl group of the ketone did not need to be adjacent to the aromatic ring for the reaction to occur, it seemed of interest to determine if compounds of the next lower state of oxidation would undergo the reaction. It was found that both phenylmethylcarbinol and its dehydration product, styrene, gave phenylacetamide in approximately the same yield as did acetophenone, under the conditions of Willgerodt and Merk.[4]

$$\begin{tikzcd} C_6H_5COCH_3 \arrow[dr] & C_6H_5CHOHCH_3 \arrow[d] & C_6H_5CH{=}CH_2 \arrow[dl] \\ & C_6H_5CH_2CONH_2 & \end{tikzcd}$$

Work on this reaction is being continued.

Experimental[5]

Yellow ammonium sulfide was prepared according to the directions of Willgerodt and Merk. Concentrated ammonium hydroxide (200 cc.) was saturated at room temperature with hydrogen sulfide. To the solution, which weighed 244 g., there was added 24.4 g. of sulfur, which was stirred into solution.

Phenylacetone was prepared by the method used by Baker[6] for 1-anisyl-2-butanone. The same material was also prepared much more easily by the method of Magidson and Garkusha.[7] When the preparation was carried out on a scale four times as large as reported by Magidson and Garkusha there was obtained, in addition to phenylacetone, b. p. 88–92° (6 mm.), 37 g. of a fraction, b. p. 171–179° (6 mm.), which gave an oxime, m. p. 119–122°. The oxime of *s*-diphenylacetone is variously reported[8] to melt from 118 to 125°.

Phenylmethylcarbinol was prepared by aluminum isopropoxide reduction of acetophenone, by the procedure of Lund[9]; the product boiled at 77–81° (5 mm.).

The styrene used was Eastman Kodak Co. White Label material.

Phenylacetone and Ammonium Polysulfide.—Phenylacetone (3.0 g.) and ammonium polysulfide (15 g.) were heated for five hours at 210 ± 5° in a pressure tube.[10] The solid material removed from the tube weighed 2.0 g. (60% crude) and melted at 86–89°; two recrystallizations of the material from water raised its melting point to 101.5°. When it was mixed with an authentic sample of

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[1] Willgerodt, *Ber.*, **20**, 2467 (1887).

[2] Willgerodt, *ibid.*, **21**, 534 (1888).

[3] Cavalieri, Pattison and Carmack, This Journal, **67**, 1783 (1945).

[4] Willgerodt and Merk, *J. prakt. Chem.*, [2] **80**, 192 (1909).

[5] Melting points and boiling points are uncorrected.

[6] Baker, This Journal, **65**, 1576 (1943).

[7] Magidson and Garkusha, *J. Gen. Chem., U. S. S. R.*, **11**, 339 (1941); *C. A.*, **35**, 5868 (1941).

[8] Beilstein, "Handbuch der organischen Chemie," 4th ed., **7**, 446 (1925); First Supplement, **7–8**, 238 (1931).

[9] Lund, *Ber.*, **70B**, 1520 (1937).

[10] The tube used was of a design suggested by Dr. J. S. Buck, Associate Director of Chemical Research of these Laboratories. An ordinary 13-inch Pyrex Carius tube was drawn down on the open end and had sealed to it an 8-inch length of 10-mm. OD-5 mm. ID Pyrex tubing. After the tube was filled the smaller tube was sealed on the end. A pressure tube of this type can be used six or eight times before another length of the smaller tubing needs to be sealed on and can be used a great many times, as contrasted with the ordinary Carius tube which has a relatively short life.