ent temperatures. Since the few known temperature coefficients of partition ratios are low, differences in temperature are not so serious a hindrance to comparison as differences in concentration. On this basis it may be said that our data for bromoacetic acid and the three chlorine-substituted acetic acids agree reasonably well with those obtained at about the same concentrations by Knaus[3] at 18° except for dichloroacetic acid. Fair agreement with the literature[2] may also be noted in our values for succinic acid and formic acid. The work of H. W. Smith,[4] for which the author indeed claimed no high accuracy, seems to be unreliable in the cases of succinic acid, tartaric acid, and probably bromoacetic acid also.

Reference to Table I shows that only glycolic acid has partition ratios which remain practically constant over the tenfold range of concentrations studied. The ratios for most other acids, including all the halogen-substituted acetic acids, decrease with increasing concentration of acid, owing partly to changing ionization in the water layer. The very large ratios for glycine, tartaric acid, and benzenesulfonic acid increase as the acid concentration increases. While this trend is probably real, the absolute values of these ratios are the least trustworthy of our measurements, for the amounts of acid in the ether layer were too small to be titrated accurately.

Experimental

Ordinary reagent grade ethyl ether was used, preliminary experiments having shown that its further purification had no effect upon partition ratios.

Most of the acids were likewise C. P. reagents, used without purification. Furoic acid was both sublimed and recrystallized, but without altering the value of the partition ratio. "Practical" dichloroacetic acid was fractionated and boiled in the open for a few minutes to expel dissolved hydrogen chloride. Benzenesulfonic acid was prepared by hydrolyzing benzenesulfonyl chloride and removing the hydrochloric acid by evaporation.[5] Acrylic acid was prepared at low temperatures and used immediately to forestall polymerization. A solution was obtained by saponifying methyl acrylate with potassium hydroxide solution at room temperatures, acidifying with hydrochloric acid, evaporating to half volume under reduced pressure at 40–50°, extracting repeatedly with ether, evaporating this to one-fifth its volume, and extracting the acid from the ether with water (70% yield).[6]

In the partition experiments, the acid solutions and the ether were mixed in glass-stoppered bottles and placed in a thermostat at 25 ± 0.2°. After at least thirty minutes the bottles were shaken vigorously for five minutes and then allowed to stand for ten minutes in the thermostat to permit complete separation of the layers. Samples were then pipetted from each layer and titrated with either 0.03219 or 0.1237 N carbonate-free standard alkali. That the time allowed for distribution and the amount of shaking were sufficient to establish equilibrium was proved by showing that increasing each did not alter the results. Phenolphthalein was used as indicator in titrating all acids except glycine, which required thymolphthalein and titration in alcoholic solution.[7] Acid in the ether layers was most easily determined by adding excess standard alkali and back-titrating with standard hydrochloric acid. Three samples of each layer were titrated at each concentration, and the mean values, along with the calculated standard deviations, were used to obtain the partition ratios and the indicated precisions of measurement.

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[3] Knaus, Thesis, Basel, Switzerland, 1923; data quoted by "Tables Annuelles," McGraw-Hill Book Co., New York, N. Y., 1924, pp. 260–262, 330.

[4] Smith, *J. Phys. Chem.*, **25**, 616 (1921).

[5] Davies and Davies, *J. Chem. Soc.*, **123**, 2976 (1923).

[6] Preparation by Mr. Jack King.

[7] Harris, *Proc. Roy. Soc.* (London), **95B**, 500 (1923).

CHEMISTRY DEPARTMENT
OKLAHOMA AGRICULTURAL AND MECHANICAL COLLEGE
STILLWATER, OKLAHOMA
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Catalysts for the Polymerization of Benzyl Chloride

BY O. C. DERMER AND EDWARD HOOPER

Many substances catalyze the reaction of benzyl chloride with itself with elimination of hydrogen chloride.[1] The catalytic activity reported for copper chloride, nickel chloride and barium chloride, which are not known to catalyze other Friedel–Crafts reactions, led us to test some anhydrous chlorides in this reaction under similar conditions. Ten ml. of C. P. benzyl chloride was placed in a dry Pyrex test-tube with a trace (pinhead size) of potential catalyst. The mixture was boiled under a "cold finger" condenser for at least two hours, or else until too little benzyl chloride was left to reflux.

One group of chlorides gave high percentages of the theoretical yield of $(C_7H_6)_x$ polymer, 86–99%, within two hours. This group includes aluminum chloride, antimony pentachloride, boron trichloride, cadmium chloride, columbium pentachloride, ferric chloride, gallium (added as metal), indium (added as metal), manganese dichloride, molybdenum pentachloride, palladium dichloride, platinum tetrachloride, stannic chloride, stannous chloride, tantalum pentachloride, titanium tetrachloride, tungsten hexachloride, uranyl acetate[2] and zinc chloride. All polymers were ther-

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[1] (a) Shriner and Berger, *J. Org. Chem.*, **6**, 305 (1941); (b) Fisher and Eisner, *ibid.*, **6**, 169 (1941).

[2] Used for lack of the chloride, but presumably converted to it in course of the reaction.

moplastic resins, varying in color from red through orange to brown or even gray-blue.

Another group produced small but perceptible amounts of polymer insoluble in the excess benzyl chloride. Here are to be named auric chloride, barium chloride, cobalt chloride, cupric chloride, lanthanum trichloride, nickel chloride, selenium tetrachloride and tellurium dichloride.

Chlorides that produced no solid polymer at all are antimony trichloride, arsenic trichloride, bismuth chloride, calcium chloride, ceric chloride, chromium chloride (either sublimed or dehydrated), iodine trichloride, lead dichloride, magnesium chloride, mercuric chloride, phosphorus trichloride, phosphorus pentachloride, silver chloride, strontium chloride, sulfur monochloride, tellurium tetrachloride, thallium trichloride and thorium tetrachloride.

It is surprising to find such a salt-like halide as manganese chloride so high in activity, and to note that the chlorides of tellurium are practically non-catalysts although the dioxide is active.[1b] Comparison with a similar survey of catalysts for the ketone synthesis,[3] although complicated by the difference in temperature used, shows a good but by no means perfect correlation between catalytic abilities of chlorides in the two reactions.

[3] Dermer, Johnson, Wilson and Dermer, THIS JOURNAL, 63, 2881 (1941).

DEPARTMENT OF CHEMISTRY
OKLAHOMA AGRICULTURAL AND MECHANICAL COLLEGE
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The Identification of Organic Acids by the Use of *p*-Bromobenzyl Pseudothiuronium Bromide

BY BARTLETT T. DEWEY AND HENRY G. SHASKY

In a previous paper from these laboratories,[1] some advantages of *p*-chlorobenzyl pseudothiuronium chloride as the reagent for the identification of organic acids were reported, and some precautions were suggested to prevent hydrolytic decompositions to which the salts are subject. *p*-Bromobenzyl pseudothiuronium bromide has since been prepared. This reagent offers some desirable qualities not found in the compounds previously reported.

The *p*-bromobenzyl pseudothiuronium bromide was prepared by refluxing 62.6 g. of *p*-bromobenzyl bromide with 19 g. of thiourea in 100 cc. of ethanol for one hour. After cooling, the *p*-bromobenzyl pseudothiuronium bromide was removed by filtration and recrystallized from ethanol. The melting point of the product was 213°. Analysis for nitrogen by the Kjeldahl method showed 8.62%; calculated, 8.59%.

Attempts to prepare polymorphous forms were unsuccessful. A portion of the original product was recrystallized by dissolving in ethanol and obtaining the crystals by chilling. The crystals obtained melted at 213°. Another portion was dissolved in 30% hydrobromic acid. The crystals obtained by slow and by rapid cooling melted at 213°. Microscopic examination revealed that the crystals obtained by all the methods were similar in form. Hydrobromic acid is not a satisfactory solvent for recrystallization because of the limited solubility of the *p*-bromobenzyl pseudothiuronium bromide.

The salts of the organic acids were obtained by adding a hot alcoholic solution of *p*-bromobenzyl pseudothiuronium bromide to an aqueous solution of the sodium or potassium salt of the acid. If the acid was used, sodium or potassium hydroxide was added to neutralize the acid. An excess of alkali did not produce rapid decomposition. The *p*-bromobenzyl pseudothiuronium salts precipitated at once in the pure state. When recrystallization was necessary, alcohol was found to be a satisfactory solvent. Boiling the alcoholic solutions for as long as one hour produced no appreciable evidence of decomposition. The salts were removed from the mother liquor by filtration. They were dried in air and over sulfuric acid for twenty-four hours. Weighed samples were then dried at 85° in a vacuum oven. No loss of weight indicative of the decomposition of hydrates was observed. The purity of the salts was established by analysis for nitrogen by the Kjeldahl method.

The high molecular weight of the reagent and the low solubility of the salts make it possible to obtain a large yield of the salt from small amounts of the acid. The formate was the only one of the thirty-seven salts prepared which did not precipitate at once. To obtain this compound, it was necessary to remove a portion of the solvent and cool to induce precipitation.

The melting points were determined in an electrically heated Thiele tube. The melting points of twenty-one aliphatic and sixteen aromatic salts are listed in the table. The melting points of the fatty acid series are not well dispersed. The salts of dibasic acids have well distributed melting points. Those containing an even number of car-

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[1] B. T. Dewey and R. B. Sperry, THIS JOURNAL, 61, 3251 (1939).