unground samples were evacuated at 290° for four hours. The surface area of the unground catalyst, as determined from the nitrogen adsorption isotherm, using the weight after evacuation, was 1061 sq. m./g., whereas that of the ground catalyst was 991 sq. m./g., a difference of 6.7%. Little, if any, effect was observed on the average Kelvin pore radius, as determined from the relative pressure corresponding to the steepest portion of the desorption curve. The unground sample had an average pore size of 21.1 A., whereas the ground sample had an average pore radius of 20.7Å.

STANDARD OIL DEVELOPMENT CO.
ELIZABETH, NEW JERSEY
RECEIVED DECEMBER 4, 1947

Preparation and Characterization of β-Dibutylaminoethyl Chloride Hydrochloride

BY HOWARD C. KLEIN[1] AND IRVING A. KAYE

β-Dibutylaminoethyl chloride hydrochloride has been prepared by the dropwise addition of 47.2 g. (0.4 mole) of thionyl chloride to 51.9 g. (0.3 mole) of β-dibutylaminoethanol, dissolved in 150 ml. of benzene. After removal of the solvent and excess thionyl chloride under diminished pressure, the tarry residue was dissolved in dry acetone, the solution decolorized with Darco G-60, and then cooled with Dry Ice. The precipitated white hydrochloride (57.9 g., 85%) melted at 86–88°.

Anal. Calcd. for $C_{10}H_{23}NCl_2$: Cl^-, 15.41; Cl (total), 30.82. Found: Cl^-, 15.30; Cl (total), 30.92.

Recrystallization of the hydrochloride from acetone–hexane gave pearly leaflets, m.p. 87–89°.

The basic chloride boiled at 119–120° (30 mm.).[2]

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(1) Nopco Chemical Company, Fine Chemicals Division, Harrison, New Jersey.

(2) Blicke and Maxwell, THIS JOURNAL, **64**, 429 (1942), found 114–115° (23 mm.).

DEPARTMENT OF CHEMISTRY
BROOKLYN COLLEGE
BROOKLYN, NEW YORK
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Synthesis of Amino-substituted Phosphonic Acids. II. α-Aminobenzylphosphonic Acid

BY GENNADY M. KOSOLAPOFF

As it was reported earlier[1] the synthesis of α-aminobenzylphosphonic acid by the reduction of *p*-nitrophenylhydrazone of diethyl benzoylphosphonate by means of hydrogen, followed by sodium sulfide, failed to yield the pure product. The contamination of the final product was caused principally by the products of incomplete reduction and led to the unusually low melting point of the substance. In order to secure the pure material it was necessary to find another reduction method which was usable in this instance. Such a procedure using the method of Fischer and Groh[2] for the reduction led to the pure substance.

The hydrazone (4 g.) in 500 cc. of ethanol was added to 10 g. of amalgamated aluminum foil immersed in 1 liter of ethanol and 200 cc. of water. The mixture was allowed to stand overnight in a loosely stoppered flask. After filtration, the precipitate was washed with 500 cc. of ethanol and the combined filtrates were treated with 300 cc. of concentrated hydrochloric acid. The solution was slowly distilled (six hours) through a Vigreux column until the volume in the still-pot amounted to approximately 50 cc. On cooling, the *p*-phenylenediamine hydrochloride was filtered off, the filtrate was evaporated to dryness by an infrared lamp and the residue was taken up in 200 cc. of ethanol. Neutralization with aniline gave the crude product which was taken up in 30 cc. of warm water, made strongly alkaline with 10% sodium hydroxide and extracted twice with 50 cc. of benzene. The aqueous solution was made just acid to congo red with 1:1 hydrochloric acid and concentrated to incipient crystallization. After cooling, the product was filtered off, washed with 5 cc. of ice-water, dissolved in 50 cc. of hot water, treated with charcoal, filtered and concentrated to 10 cc. On cooling there was obtained 1.0 g. (50%) of *dl*-α-aminobenzylphosphonic acid, in the form of tiny bunched colorless needles, which melted at 272–273°.

Anal. Calcd.: N, 7.5; P, 16.6. Found: N, 7.46; P, 16.7.

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(1) Kosolapoff, THIS JOURNAL, **69**, 2112 (1947).

(2) Fischer and Groh, *Ann.*, **383**, 363 (1911).

CENTRAL RESEARCH DEPARTMENT
MONSANTO CHEMICAL COMPANY
DAYTON 7, OHIO
RECEIVED SEPTEMBER 27, 1947

Copolymerization Rate Constants in the System 2,5-Dichlorostyrene–Methyl Acrylate

BY F. LEONARD, W. P. HOHENSTEIN AND E. MERZ

During the course of an investigation of the copolymerization of the isomeric dichlorostyrenes and acrylic esters, it became of interest to determine the copolymerization rate constants in the system 2,5-dichlorostyrene and methyl acrylate. The results of this determination are herein presented.

Experimental

2,5-Dichlorostyrene.—This monomer was obtained from the Monsanto Chemical Co. and was purified by washing with 5% sodium hydroxide solution and then with distilled water until the washes were neutral to litmus. The monomer was allowed to dry over calcium chloride overnight. It was then filtered and checked for the presence of polymer by adding a sample to methanol. If no turbidity was observed, the monomer was used *per se*.

Methyl Acrylate.—This monomer obtained from Rohm and Haas was distilled *in vacuo* through a 12″ column packed with glass helices in an all-glass system. The first 10 cc. to distil was rejected and a residue of 50 cc. was left in the distilling flask.

Polymerization and Purification.—The requisite quantities of 2,5-dichlorostyrene, methyl acrylate and benzoyl peroxide (0.5% by weight based on monomers) were weighed into Pyrex glass test-tubes. The tubes were sealed, and immersed in a water-bath held at 70 ± 0.1°. The per cent. conversion was estimated approximately by the rate of rise of air bubbles through the polymerizing mixture when the tubes were inverted. When it appeared that the desired conversion, <5%, had been reached, the tubes were immediately chilled, and the seal broken. The contents of the tubes were dissolved in methyl ethyl ketone containing hydroquinone, and this solution was slowly added with stirring to a 3 times excess of methanol. The precipitated polymer was filtered, washed copiously with methanol and allowed to dry to constant weight in a vacuum oven at 60°.

Chlorine Analysis.—The per cent. chlorine was determined using the Parr bomb.

Results and Discussion

The experimental data are summarized in Table I. The copolymerization rate constants were calculated according to the method of Alfrey and Goldfinger[1] in the usual manner.

TABLE I

DETERMINATION OF r_1 AND r_2

THE COPOLYMERIZATION RATE CONSTANTS SYSTEM 2,5-DICHLOROSTYRENE–METHYL ACRYLATE

Monomer composition				Polymer composition (Exp.)	
Mole fraction 2,5-dichlorostyrene	Mole fraction methyl acrylate	Yield, %	Chlorine, %	Mole fraction 2,5-dichlorostyrene	Mole fraction methyl acrylate
0.90	0.10	4.4	39.95	0.950	0.050
.75	.25	3.0	39.15	.913	.087
.50	.50	3.7	37.20	.829	.171
.25	.75	4.4	32.15	.643	.357
.10	.90	4.9	22.30	.371	.629
.05	.95	4.3	14.15	.206	.794

The smooth curve in Fig. 1 represents the theoretical curve calculated from the values $\alpha = 0.25$ and $\beta = 0.15$. These correspond to the values, according to the latest nomenclature,[2] $r_1 = 4$ and $r_2 = 0.15$, respectively. The encircled points are experimentally determined from the data in Table I.

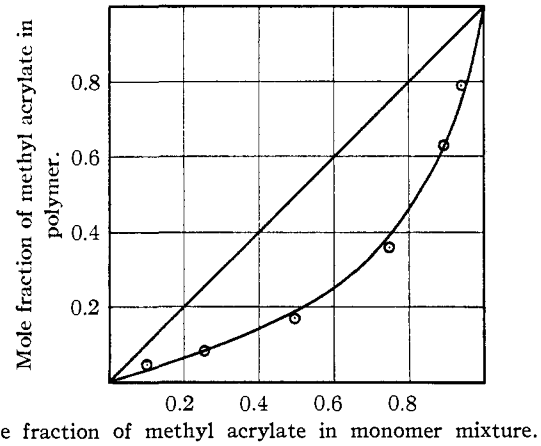

Fig. 1.—Copolymerization composition curve.

The value $r_1 = 4$ indicates that the 2,5-dichlorostyrene monomer adds to the 2,5-dichlorostyrene free radical four times as fast as the methyl acrylate monomer adds. The value $r_2 = 0.15$ indicates that the methyl acrylate monomer adds to the methyl acrylate free radical 0.15 as fast as the 2,5 dichlorostyrene monomer adds to the methyl acrylate free radical.

POLYTECHNIC INSTITUTE OF BROOKLYN
BROOKLYN, N. Y.
RECEIVED OCTOBER 20, 1947

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[1] T. Alfrey and G. Goldfinger, *J. Chem. Phys.*, **12**, 205 (1944).

[2] Alfrey, Mayo and Wall, *J. Polymer Sci.*, **1**, 581 (1946).

The Preparation of 2,3,5-Triphenyltetrazolium Chloride

BY A. M. MATTSON, C. O. JENSEN AND R. A. DUTCHER

Synthesis of 2,3,5-triphenyltetrazolium chloride by the method of Pechman and Runge as modified by Bamberger and Billeter and by Kuhn and Jerchel[1] resulted in poor yields of preparations which had a greater chloride content than the desired monobasic compound. A better yield of the compound with the theoretical chloride content and a saving of time were achieved by modifying the previous procedures.

Experimental

Triphenylformazan.—Twenty-one and two-tenths grams (0.2 mole) of freshly distilled benzaldehyde was dissolved in 125 ml. of methanol. To this solution 21.6 g. (0.2 mole) of phenylhydrazine was added during mechanical agitation. The hydrazone, dissolved in one liter of methanol, was added to a solution of 50 g. of sodium hydroxide and 70 g. of sodium acetate in one liter of methanol. To this solution, cooled to 20°, benzenediazonium chloride prepared from 18.6 g. of aniline (0.2 mole), 50 ml. of concentrated hydrochloric acid, 50 ml. of water and 14–15 g. of sodium nitrite, was added slowly during agitation. Formazan was precipitated as small red crystals. A yield of 15.8 g. (23%) of triphenylformazan was obtained, m. p. 170°.

2,3,5-Triphenyltetrazolium Chloride.—Fifteen grams (0.05 mole) of triphenylformazan were dissolved in 100 ml. of chloroform and the solution was cooled to 20°. Lead tetraacetate (30 g.) was added until the red color disappeared. The chloroform was evaporated and the residue taken up in water. Hydrochloric acid was added and the lead chloride was removed by filtration. The monobasic triphenyltetrazolium chloride was removed from the filtrate by three successive extractions with chloroform (water–chloroform ratio of 3:1), leaving the more acid salt in the water. The chloroform solution was concentrated on the steam-bath. Addition of ether to this solution precipitated the tetrazolium salt in long, silky needles. Nine and seven-tenths grams (57.7% based on formazan) of 2,4,5-triphenyltetrazolium chloride was obtained, m. p. 245° (d.) (Pechman and Runge 243°).

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[1] Pechman and Runge, *Ber.*, **27**, 2920 (1894); Bamberger and Billeter, *Helv. Chim. Acta*, **14**, 232 (1931); Kuhn and Jerchel, *Ber.*, **74B**, 941 (1941).

FREAR LABORATORIES
THE PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PENNSYLVANIA
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Effects of Inhibitors on the Polymerization of Styrene[1]

BY FRANK R. MAYO AND R. A. GREGG

Inhibitors of free radical polymerization are regarded as materials which, by transfer or addition, are converted to radicals so stable they do

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[1] This paper was presented before the Division of Organic Chemistry at the New York City Meeting of the American Chemical Society, September 15, 1947.