[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE COLLEGE OF ARTS AND SCIENCES OF THE UNIVERSITY OF LOUISVILLE]

Preparation and Polymerization of *p*-Sulfonamidostyrene[1]

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p-Sulfonamidostyrene, prepared by dehydrohalogenation of its β-bromoethyl derivative, has been characterized and polymerized. The starting material in the synthesis, β-bromoethylbenzene, is chlorosulfonated and converted without isolation of the sulfonyl chloride to β-bromoethylbenzenesulfonamide. The product has been identified as the *p*-isomer by oxidation to the known *p*-sulfonamidobenzoic acid. Polymerization by bulk, solution, and emulsion techniques gives both insoluble polymers and polymers soluble in dilute sodium hydroxide and pyridine. The soluble polymers have limiting viscosities of 0.145 to 1.3. On titration in 50% aqueous dimethylformamide solution, the polymer behaves as a monobasic acid with a capacity of 4.78–5.58 meq./g. The polymer can be hydrolyzed with nitrous acid.

The ion exchange capacity of sulfostyrene polymers prepared by the sulfonation of polystyrene is limited by the degree of sulfonation which can be achieved without extensive degradation of the polymer. Currently available polymers are variously stated to have capacities of 4.2–4.58[3] and 4.5–5.0[4] meq./g. of resin. This corresponds to something less than one sulfo group per styrene unit for which the theoretical capacity is 5.4 meq./g. of resin. One method of overcoming this limitation is to introduce the sulfo group or groups in the monomer prior to polymerization. The present investigation was undertaken to develop this route to sulfostyrene ion exchange resins of increased capacity. As part of this program we wish to report the results of a study of the preparation and polymerization of *p*-sulfonamidostyrene and some characteristics of the polmyer obtained.

Previous surveys of substituted styrenes[5,6,7] have reported only two monomeric sulfostyrene derivatives. These are N,N-dimethylsulfonamidostyrene[8] and *p*-sulfonamidostyrene.[9] There is no description in the literature of synthetic details or characterization data for *p*-sulfonamidostyrene or any physical characterization data for its polymer.

p-Sulfonamidostyrene, m.p. 138–139°, was prepared by dehydrohalogenation of β-(*p*-sulfonamidophenyl)-ethyl bromide. The bromide was prepared by chlorosulfonation of β-phenylethyl bromide to give the sulfonyl chloride which was converted without isolation to the sulfonamide. This amide was dehydrohalogenated to the styrene on refluxing with alcoholic potassium hydroxide. The product has been identified as *p*-sulfonamidostyrene by oxidation to the known *p*-sulfonamidobenzoic acid.[10] The styrene has also been identified as its dibromide.

p-Sulfonamidostyrene polymerizes readily under a variety of conditions. Heated at its melting point (135–140°), it is converted to a hard, glassy solid insoluble in all solvents tested. A small fraction of soluble material can be extracted from the polymer with 1% sodium hydroxide, but the bulk of the polymer is insoluble. Some of the polymers swell in the presence of dilute sodium hydroxide. Bulk polymers prepared at 140° with 0.1% *t*-butyl peracetate as initiator have similar properties. By conducting the bulk polymerization at 165° in the presence of 20% *t*-butyl peracetate, a low molecular weight polymer, soluble in pyridine and 0.1 *N* (and 1%) sodium hydroxide, was obtained.

Solution polymerization takes place readily on refluxing saturated (1%) ethylbenzene solutions with 0.1–15% *t*-butyl peracetate initiator. The polymerization is substantially complete within 15 minutes. The polymer precipitates from solution as a white powder with solubility characteristics dependent on the amount of initiator used. With 15% of initiator the polymer is soluble in pyridine and 0.1 *N* sodium hydroxide; with 5–10%, insoluble in pyridine but soluble in 0.1 *N* sodium hydroxide; and with 1% or less, substantially insoluble in all solvents tested.

The viscosity of those solution polymers soluble in pyridine and in dilute sodium hydroxide is low. Viscosities have been determined on pyridine and 0.094 *N* sodium hydroxide solutions. The specific viscosities range from 0.09 to 0.21 for solutions of 0.6 to 0.7 g. of polymer per 100 ml. of either solvent. These data indicate that polymers prepared by solution or bulk techniques become highly cross-linked at a low degree of polymerization. The plots of specific viscosity divided by concentration against concentration are irregular except for that of the highest viscosity, soluble polymer; that prepared with 5% initiator. The plot of the data for this polymer shows a positive slope and extrapolates linearly over the concentration range studied to a limiting viscosity of 0.145 at concentration zero. There is no real indication in these data of the pronounced increase in viscosity on dilution that has been observed with the viscosity data for solutions of polyelectrolytes.[11]

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[2] Pre-doctoral research assistant. The authors are indebted to Mr. J. P. Johansen for assistance with the viscosity measurements.

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This may possibly be due to cross-linking between sulfonamide groups with resultant modification of the ionic characteristics of the polymers.

An emulsion polymer formed on polymerization with persulfate–bisulfite initiator at 45° is soluble in both pyridine and 1% sodium hydroxide and has a relative viscosity of 1.14 (0.126 g. per 100 ml. of pyridine). The viscosity plot shows a marked increase at decreased concentration. This polymer dissolved in excess alkali and dimethylformamide titrates in solution as a weak acid. The break in the titration curve is not distinct but occurs well within the *p*H 6–7 (apparent) range indicating a capacity of 4.78–5.58 meq./g. of dry polymer. Further characterization of this polymer is in progress.

The dehydrohalogenation of α-haloethylbenzenesulfonic acid derivatives to vinyl compounds although it represents a standard reaction and has been suggested as a satisfactory synthesis using chloro types,[9] has been uniformly unsuccessful in our studies using α-bromoethyl types. The reaction takes a different course which will be described in another report.

Experimental

β-(*p*-Sulfonamidophenyl)-ethyl Bromide.—To 783 g. (6.78 moles) of chlorosulfonic acid in a 2-liter three-necked flask equipped with stirrer, dropping funnel and outlet vapor trap was added 250 g. (1.35 moles) of β-phenylethyl bromide over a period of 2.75 hours. The temperature was held below 27° by external cooling with an ice-bath. After another hour, the mixture was poured over a large quantity of ice, and the aqueous layer was decanted. The semi-solid product was triturated in ice-water and separated by decantation. The crude sulfonyl chloride was slowly introduced into an excess of ammonium hydroxide with stirring. The solution was heated for 15 minutes and the mixture allowed to stand overnight. The solid was collected on a filter, washed with water and dried. The yield of crude amide, m.p. 163–167°, was 289 g. (1.09 moles) or 81%. The crude amide was recrystallized first from an ethanol–water mixture and then from benzene, m.p. 185–186°, reported m.p. 185.5–6°.[8]

Anal. Calcd. for $C_8H_{10}O_2SNBr$: N, 5.31; S, 12.13. Found: N, 5.20; S, 12.17.

***p*-Sulfonamidostyrene.**—To 125 ml. of ethanol containing 2.66 g. of potassium hydroxide in a round-bottom flask equipped with a Glascol mantle and magnetic stirrer was added 5 g. of β-(*p*-sulfonamidophenyl)-ethyl bromide. The solution was refluxed for 3/4 hour with a trace of hydroquinone. The solution was cooled and then acidified with 100 ml. of a (1–9) concentrated hydrochloric acid–water mixture and filtered. The filtrate was extracted three times (100 ml. each) with ether. The ether was removed in a vacuum. No air was allowed to flow through the ether solution. The precipitate and the product from the ether extract were combined and recrystallized from benzene to give 1.48 g. or 43% of product, m.p. 138–139°. The monomer polymerizes on standing at room temperature but not readily on boiling in benzene with benzoyl peroxide. A low melting isomer, m.p. 110–111°, has been obtained from the mother liquors.

Anal. Calcd. for $C_8H_9O_2SN$: N, 7.65; S, 17.50; neut. equiv., 183. Found: N, 7.61; S, 17.46; neut. equiv., 178.

The monomer was recrystallized from ethanol just before use in polymerization experiments to remove a small amount of insoluble polymer which forms when the monomer is stored for a short time.

Oxidation of *p*-sulfonamidostyrene, m.p. 138–139°, with aqueous permanganate gave a solid product which melts with dec. at 273–274°. The reported m.p.'s of sulfonamidobenzoic acids are for the ortho 153–155°; for the meta 237°; for the para 280° with dec.[10]

***p*-Sulfonamidostyrene Dibromide.**—To 0.1 g. of the *p*-sulfonamidostyrene dissolved in benzene was added a small quantity of a solution of bromine in benzene. The mixture was allowed to stand overnight and then was evaporated to dryness. The residue was recrystallized several times from a (1–1) ethanol–water mixture to give a product, m.p. 170–171°.

Anal. Calcd. for $C_8H_9O_2SNBr_2$: N, 4.08. Found: N, 4.14.

Bulk Polymerization.—The monomer was polymerized by heating in a sealed tube under nitrogen. With no added initiator or with 0.1% of *t*-butyl peracetate, a polymer insoluble in all solvents tested was obtained. A minor fraction of the polymer was extractable with 1% sodium hydroxide. With 20% of *t*-butyl peracetate, a polymer soluble in pyridine and in 1% sodium hydroxide was obtained.

Solution Polymerization.—To 1500 ml. of ethylbenzene was added 12 g. of *p*-sulfonamidostyrene. The solution was heated to boiling. To this solution was added 20 ml. of a catalyst solution prepared by dissolving 5 ml. of *t*-butylperacetate[12] in 50 ml. of ethylbenzene. Two ml. additional of the catalyst solution was added after 10 minutes of refluxing. After refluxing for an additional 5 minutes, the precipitated polymer was collected on a filter and washed with boiling ethanol. A yield of 11 g. or 91.6% of the polymer was obtained.

Anal. Calcd. for $(C_8H_9O_2SN)_x$; N, 7.65. Found: N, 7.30.

Other solution polymers were prepared similarly but in smaller quantities (0.2–0.9 g. of monomer in 10–100 ml. of ethylbenzene) using 0.1, 1, 5 and 10% of *t*-butyl peracetate initiator. The solubilities and viscosity characteristics of these polymers are given in Table I.

TABLE I

Initiator, %	Yield of polymer, %	Solubility[a] 0.1 *N* NaOH	Solubility[a] Pyridine	Relative viscosity[b]
0.1	28	Ins.	—	—
1	80	Ins.	—	—
5	62	Sol.	Ins.	0.21 N
10	75	Sol.	Ins.	.17 N
15	91.6	Sol.	Sol.	.11 P
15	—	Sol.	Sol.	.19 N

[a] Insoluble polymers usually swell in dil. sodium hydroxide and usually contain a small fraction extractable with alkali. [b] At approximately 0.6 g./100 ml. of solvent; N, 0.094 *N* NaOH; P, pyridine.

No polymer was obtained on refluxing the monomer with benzoyl peroxide in thiophene-free benzene, ethanol or acetone. After one-half hour reflux periods, the monomer was recovered in 91–100% yields. A 2-g. sample of solution polymer prepared with 15% initiator was suspended in an aqueous solution of 3 g. of sodium nitrite. To this was added 5 ml. of concd. hydrochloric acid diluted with 5 ml. of water. After 48 hours a second addition and after 24 hours a third addition of sodium nitrite and acid was made. The polymer was collected on a filter, washed with water, and dried. Nitrogen analysis (Dumas) gave 1.32% nitrogen which is equivalent to 82% hydrolysis of the sulfonamide to sulfonic acid.

Emulsion Polymerization.—To 11.9 g. of the monomer, m.p. 138–139°, was added 120 ml. of distilled water containing 1.4 g. of Dupanol ME. The water mixture was stirred under an oxygen-free nitrogen atmosphere. The solution was brought to 45°, and then 20 ml. of water containing 0.4 g. of potassium persulfate and 0.2 g. of sodium bisulfite was added. The emulsion was stirred for 5 hours at 45°. The polymer which precipitated during this time was collected on a filter, washed with water, dilute hydrochloric acid, water and finally ethanol, and then dried. A yield of 11 g. or 92.3% of polymer was obtained. The polymer was soluble in 10% sodium hydroxide. A sample of the polymer was dissolved in 0.05137 *N* sodium hydroxide. An aliquot portion was diluted with five volumes of dimethylformamide and titrated with 0.05209 *N* hydrochloric acid. The break in the curve was not distinct. The differential plot showed clearly an inflection point between limits indi-

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(12) Used as supplied by the Lucidol Division. The authors wish to thank the Lucidol Division for supplying samples.

cating a capacity of 4.78–5.58 meq./g. of polymer. This polymer has relative viscosities in pyridine of 1.140 (0.126 g./100 ml.); 1.08 (0.063 g./100 ml.) and 1.04 (0.032 g./100 ml.).

Viscosity Measurements.—The polymers were dissolved in J. T. Baker C.P. pyridine or in 0.094 *N* sodium hydroxide and the solutions filtered. The viscosities were measured in Ostwald viscometers at 30° at successive dilutions starting with solutions of 0.4–0.6 g. per 100 ml. of solvent in most determinations.

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The Stereochemistry of the Formation and Decomposition of Dimethyl-α-phenethylsulfonium Bromide[1,2]

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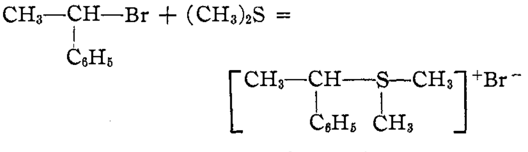
The formation of dimethyl-α-phenethylsulfonium bromide from methyl sulfide and α-phenethyl bromide, and its decomposition, proceed with the predominant inversion of the asymmetric carbon atom. The reaction takes place in a medium of low polarity, the liquid reactants, at 23°. Kinetic evidence points to a homogeneous reaction although the salt has a low solubility in the reaction medium. The significance of these results for the theory of the displacement reaction is discussed.

Although the displacement of a halide ion from an alkyl halide in a polar solvent, by reagents such as sodium iodide, is clearly accompanied by inversion of configuration,[4] it is not so evident that all one-stage displacement reactions must occur with this steric result.[5] In particular, a displacement reaction between two reactants of such a type that a large separation of charge must appear in the transition state, is one which might take place with retention of configuration. However, the thermal decomposition of D-(+)-N,N,N-trimethyl-α-phenethylammonium acetate yields a product with an inverted configuration[6] as does the decomposition of 1-piperityltrimethylammonium hydroxide.[7] These observations have been cited in support of a quantum mechanical argument for a nearly linear arrangement of the reaction centers in the transition state of all displacement reactions.[8] But the argument is weakened by the fact that the decomposition occurs in a fused salt, a medium equivalent to one with a high dielectric constant, and one which would certainly tend to minimize electrostatic effects.

It appeared to us that if electrostatic interactions could influence the course of a displacement reaction from one of inversion of configuration (the usual result) to retention of configuration, then such an effect would be most pronounced if the reaction occurred in a solvent having a low dielectric constant. A suitable reaction appeared to be that of α-phenethyl bromide with methyl sulfide to form a sulfonium salt, or the reverse process.



$$CH_3—\underset{C_6H_5}{CH}—Br + (CH_3)_2S = \left[CH_3—\underset{C_6H_5}{CH}—\underset{CH_3}{S}—CH_3\right]^+Br^- \quad (1)$$

The reactants on the left are low in polarity and can themselves provide the appropriate medium. By the use of the principle of microscopic reversibility, one may conclude that if the formation of the sulfonium salt proceeds with inversion of configuration then the reverse process should likewise proceed with inversion, the converse being equally true.

The conditions for the formation of this salt from the above reagents and, alternatively, from methyl α-phenethyl sulfide and methyl bromide were studied systematically. Substantially pure dimethyl-α-phenethylsulfonium bromide was isolated and characterized, and information to guide the subsequent studies with the optically active reagents was collected.

The stereochemistry of the forward reaction was studied directly by the isolation of the active salt from active α-phenethyl bromide and methyl sulfide and the stereochemistry of the reverse reaction was studied indirectly by allowing the salt, formed from active methyl α-phenethyl sulfide and methyl bromide, to decompose in the presence of an excess of the latter. These conditions served to drive the reaction in the desired direction by the removal of methyl sulfide as the insoluble trimethylsulfonium bromide.

Experimental[9]

α-Phenethylisothiouronium Bromide.—A mixture of α-phenethyl bromide[10] (137.0 g.), thiourea (56.4 g.) and 95% ethyl alcohol (375 ml.) was refluxed for six hours. The solvent was removed by distillation under reduced pressure. An equal volume of anhydrous benzene was added to the hot residue, and the mixture was swirled until crystallization had begun and finally chilled to 0°. The solid was filtered and washed repeatedly with absolute ether until the washings were colorless, and dried at 70°; yield 177.6 g. (91.8%), m.p. 153–157°. A small sample of the material

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[1] From the dissertation of Allen F. Graefe, submitted in partial fulfillment of the requirements for the Ph.D. degree at Illinois Institute of Technology, February, 1952.

[2] Presented at the 121st National Meeting of the American Chemical Society, Milwaukee, Wis., March 31, 1952.

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