

Preparation of *m*-Divinylbenzene¹

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In connection with the testing of divinylbenzenes as cross-linking agents in emulsion polymerization an improved synthesis of *m*-divinylbenzene has been developed. *m*-Xylene was oxidized to isophthalaldehyde by chromic anhydride in a mixture of acetic anhydride and sulfuric acid, according to a modification of the procedure of Thiel and Winter.² The aldehyde was converted to bis-*m*-(α -hydroxyethyl)-benzene by a method similar to that of Deluchat,³ using a large excess of methylmagnesium iodide in a mixture of ether and benzene. The carbinol was then converted to the diacetate, which was pyrolyzed to give a good yield of *m*-divinylbenzene.

Experimental

Isophthalaldehyde.—In a 2-liter, three-necked, round-bottomed flask equipped with stirrer, dropping funnel and a thermometer extending nearly to the bottom of the flask were placed 25 g. (0.231 mole) of *m*-xylene, 1 kg. (928 cc.) of acetic anhydride and 400 g. (382 cc.) of glacial acetic acid. The reaction mixture was stirred and kept at 5–10° while 150 g. (83 cc.) of concentrated sulfuric acid was added slowly. Over a period of one and one-half hours 90 g. (0.9 mole) of chromic anhydride was added cautiously in small amounts, so that the reaction temperature did not exceed 10°. After the addition was complete stirring was continued for two to three hours at 5°.

The reaction mixture was poured rapidly onto 2 liters of cracked ice, with vigorous stirring, and extracted with three 250-cc. portions of chloroform. These extracts were kept separate and used to wash the decomposition mixture from a second experiment which was run in exactly the same way. The extracts were then combined and washed twice with water to remove most of the acid. It was not desirable to neutralize the chloroform solution. The solution was dried and the drying agent filtered off and the solvent removed under reduced pressure, care being taken to keep the temperature below 40°.

One hundred cc. of water and 10 cc. of 85% phosphoric acid were added and the mixture steam distilled. The first 10–15 cc. of distillate (chloroform) was discarded. Approximately 4 liters of distillate was then collected and chilled overnight in an ice box. Filtration produced 10 g. of isophthalaldehyde, m. p. 84–87°.

The aqueous filtrate was extracted with chloroform, the solvent removed under reduced pressure, and the residue recrystallized from alcohol and water. The total yield was 18–19.5 g. (29–31%). After successive recrystallizations the product melted at 89°. Thiel and Winter² reported m. p. 89°.

bis-*m*-(α -Hydroxyethyl)-benzene.—A standard Grignard procedure was used, with modifications. When the methylmagnesium iodide had been prepared in ether solution most of the ether was distilled and 600 cc. of dry benzene added. The aldehyde, in benzene solution, was added at reflux temperature. During this addition the benzene which refluxed was removed from the reaction mixture at such a rate that the volume of the reaction mixture remained constant. Decomposition and isolation of the crude product was accomplished in the usual way. The resulting oil was dissolved in ether. Crystallization was promoted by the careful addition of low boiling petroleum ether and cooling. From 313 g. (2.1 moles) of

methyl iodide, 50 g. (2.1 moles) of magnesium, and 50 g. (0.37 mole) of isophthalaldehyde there was obtained 25 g. (40%) of impure product, m. p. 90°. Recrystallization gave pure bis-*m*-(α -hydroxyethyl)-benzene, m. p. 98°. Deluchat³ reported m. p. 98°.

Lower ratios of methylmagnesium iodide to aldehyde gave lower yields.

bis-*m*-(α -Hydroxyethyl)-benzene Diacetate.—Seven hundred cc. (7.4 moles) of acetic anhydride, 65.3 g. (0.39 mole) of bis-*m*-(α -hydroxyethyl)-benzene, and 10 cc. of pyridine were mixed, heated for four hours on a steam cone, let stand overnight and distilled. The yield of diacetate was 91.7 g. (93.5%), b. p. 149–150° (3 mm.), n_D^{20} 1.4932, d_4^{20} 1.0810.

Anal. Calcd. for $C_{11}H_{18}O_4$: C, 67.18; H, 7.25. Found: C, 67.73; H, 7.13.

***m*-Divinylbenzene.**—The pyrolysis of 64.3 g. (0.26 mole) of the diacetate was effected by dropping it through an 18-mm. Pyrex tube packed for 20 cm. with glass beads and heated to 600°. During the reaction, a slow stream of nitrogen was used to flush the pyrolysate into the receiver. A trace of picric acid was added and the crude product distilled to yield 27.1 g. (86%) (based on unrecovered acetate) of *m*-divinylbenzene, b. p. 52–54° (2 mm.), n_D^{20} 1.5760, and 3.8 g. of unchanged acetate. Deluchat³ reported b. p. 52° (3 mm.), n_D^{20} 1.5745, d_4^{20} 0.926.

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The Electrical Conductance of Aqueous Solutions. IV. Silver Chlorate at 25°

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The electrical conductances of dilute aqueous silver chlorate were measured in 1888 by Loeb and Nernst.¹ This investigation repeats these measurements at 25.00 \pm 0.010 and extends the concentration range studied to about 0.3 molar. The apparatus, methods of calibration, temperature control, cells, etc., have all been described previously.² The silver chlorate was prepared by the directions of Nicholson and Holley.³ It was analyzed for purity against a standard sodium chloride solution by weight titrations using dichlorofluorescein as adsorption indicator. After four recrystallizations from water, two separate preparations gave average analyses of 100.06 and 99.95% pure. Solutions of the same concentration made from these two samples showed no appreciable difference in the molar conductances. All solutions were prepared by weighing the dry salt and water, or by weight dilution from a more concentrated solution. The data obtained are collected in Table I.

The densities of these solutions were taken in 25-ml. pycnometers. Up to concentrations of about 16 g./1000 g. of solution, the measurements are linear and conform within 0.01% to the equation

$$d = 0.99707 + 0.000807 \text{ g./1000 g. of soln.}$$

(1) This work was done under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

(2) Thiel and Winter, *Ann.*, **311**, 359 (1900).

(3) Deluchat, *Ann. chim.*, [11] **1**, 181 (1934).

(1) Loeb and Nernst, *Z. physik. Chem.*, **2**, 948 (1888); "International Critical Tables," Vol. IV, p. 244.

(2) J. H. Jones, *This Journal*, **68**, 240 (1946).

(3) "Inorganic Syntheses," Vol. II, p. 4–6.

TABLE I
CONDUCTANCES OF SILVER CHLORATE SOLUTIONS

| C | C ^{1/2} | Λ |
|-----------|------------------|--------|
| 0.0010256 | 0.03202 | 123.43 |
| .0013694 | .03700 | 122.94 |
| .0029782 | .05457 | 121.14 |
| .0032500 | .05701 | 120.95 |
| .006693 | .08181 | 118.57 |
| .007223 | .08499 | 118.29 |
| .011165 | .10567 | 116.38 |
| .020409 | .14286 | 113.05 |
| .025945 | .16110 | 111.52 |
| .029471 | .17167 | 110.70 |
| .030005 | .17322 | 110.57 |
| .045927 | .21421 | 107.33 |
| .061064 | .24711 | 104.82 |
| .085240 | .29196 | 101.58 |
| .092665 | .30441 | 100.80 |
| .13630 | .36920 | 96.50 |
| .19945 | .4466 | 91.90 |
| .28488 | .5336 | 87.15 |

The limiting conductance of silver chlorate was found by two methods. A large-scale plot of Λ vs. $C^{1/2}$ gave a limiting value of $\Lambda_0 = 126.62$ with a slope of 99.96. A plot of the Shedlovsky function⁴ $\Lambda'_0 = (\Lambda + \beta C^{1/2})/(1 - \alpha C^{1/2})$ vs. C , gave a value of 126.53. The Shedlovsky plot showed the typical low slope and deviation from a linear relationship found previously in many silver, potassium and thallium salts. The slope was lower (31.7) and the deviation larger than for potassium salts. An average value of $\Lambda_0 = 126.57$, together with the known ionic conductance of the silver ion (61.92) will yield a value of 64.65 for the ionic conductance of the chlorate ion. Up to 0.08 m , with two exceptions, the experimental points are within 0.02% of the smoothed curve through the points for the Shedlovsky function plot. The accuracy in the evaluation of Λ_0 should be greater than 0.1%. The data of Loeb and Nernst, although not consistent, would extrapolate (Λ vs. $C^{1/2}$) to approximately the same value as reported here but their slope was only 67 and hence the individual measurements vary more and more as concentration increases. The only other value found for the ionic conductance of the chlorate ion is that of 63.13, computed from the conductance at 18° and the temperature coefficient listed in the "International Critical Tables."⁵

(4) T. Shedlovsky, *THIS JOURNAL*, **54**, 1405 (1932).

(5) "International Critical Tables," Vol. VI, p. 23.

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Isotonic Solutions: Activity Coefficients of Potassium Bromate at 25°

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Measurements have been completed in this Laboratory on the concentrations of solutions of

potassium bromate and sodium chloride that are isotonic. The apparatus and procedure have been previously described.¹ The potassium bromate was purified by crystallization from redistilled water, dried at 180° in platinum, and stored in a vacuum desiccator over anhydrous. The purification of sodium chloride has been previously described.¹ All solutions were prepared directly from weighed amounts of salt and water. The data are collected in Table I.

TABLE I
CONCENTRATIONS OF ISOTONIC SOLUTIONS

| m_{KBrO_3} | Ratio | m_{NaCl} | ϕ_{KBrO_3} |
|---------------------|--------|-------------------|------------------------|
| 0.2077 | 0.1977 | 0.9520 | 0.8802 |
| .2188 | .2081 | .9510 | .8789 |
| .2204 | .2090 | .9483 | .8764 |
| .2246 | .2128 | .9474 | .8755 |
| .2840 | .2657 | .9355 | .8616 |
| .3198 | .2965 | .9271 | .8543 |
| .4117 | .3740 | .9084 | .8363 |
| .4266 | .3865 | .9060 | .8337 |
| .4274 | .3876 | .9064 | .8345 |
| .4744 | .4267 | .8894 | .8280 |

From these data and the published values for sodium chloride,² the osmotic coefficients, ϕ , for potassium bromate were computed. Using the computed values of the osmotic coefficients in the equation

$$-\ln \gamma_{\pm} = 1 - \phi + 2 \int_0^m \frac{1 - \phi}{m^{1/2}} dm^{1/2}$$

the activity coefficients of potassium bromate were calculated. The integral was evaluated graphically from a large scale plot of $(1 - \phi)/m^{1/2}$ vs. $m^{1/2}$. The values of the d parameter (distance of closest approach of the ions) varied almost linearly with concentration, having a value of 1.96 Å. at 0.2 m and 1.49 Å. at 0.45 m . The extrapolation of the above plot to infinite dilution was made by finding a value of d (2.6 Å.) which made the deviations between the observed and calculated values of the function $(1 - \phi)/m^{1/2}$ proportional to the concentration for the experimental points. This same proportional variation was assumed to hold to infinite dilution. The osmotic and activity coefficients at rounded concentrations are tabulated in Table II.

TABLE II
ACTIVITY AND OSMOTIC COEFFICIENTS OF POTASSIUM BROMATE

| m | ϕ | γ_{\pm} (KBrO ₃) | γ_{\pm} (KClO ₃) |
|------|--------|-------------------------------------|-------------------------------------|
| 0.15 | 0.8944 | 0.702 | |
| .20 | .8813 | .671 | 0.678 |
| .25 | .8693 | .644 | |
| .30 | .8590 | .622 | .632 |
| .35 | .8488 | .602 | |
| .40 | .8393 | .584 | .596 |
| .45 | .8310 | .568 | |
| .50 | .8225 | .553 | .566 |

(1) James Homer Jones, *THIS JOURNAL*, **65**, 1353 (1943).

(2) Stokes and Levien, *ibid.*, **68**, 337 (1946).