complexity constants are much higher in the copper than in the chromium system, it can be concluded that the 3rd formation constant must be exceedingly small in the last mentioned case. Also the relatively small "pentammine" effect in the chromous system gives evidence for this.

Experimental. Chromous solutions were prepared by dissolving electrolytically purified chromium metal (kindly furnished by E. I. du Pont de Nemours and Co.) in hot oxygenfree hydrochloric acid to give solutions containing ca. 0.2 M chromous chloride and 0.2 M hydrochloric acid. Chromium(II) was determined by titration with potassium iodate⁸, hydrochloric acid by potentiometric titration with sodium hydroxide, and chromium(III) spectrophotometrically. The solution used contained less than 2 % of the chromium as chromic ion which was ignored. The chromium(II) solution was always under a positive pressure of nitrogen, and all other solutions were made oxygenfree by bubbling with nitrogen. The ethylenediamine hydrate was specially purified by Carbide and Carbon Chemicals Company and distilled through a column. It was diluted with an equal volume of 2 M potassium chloride and swept with nitrogen before use.

The titrations were performed under nitrogen in a thermostated cell at 25°C. The cell E.M.F. was measured with a Radiometer pH meter, model PHM 3, using a glass electrode which had been tested for linear response to pH. The acidity constants of the ethylenediamine ($pK_{\text{enH}_2} = 7.44$, $pK_{\text{enH}} = 10.06$) were determined by titrating solutions of the same composition as for the complexity titrations, replacing the chromous chloride with an equivalent amount of barium chloride².

1. Bjerrum, J. and Jørgensen, C. K. *Rec. trav. chim.* **75** (1956) 658.
2. Bjerrum, J. *Metal Ammine Formation in Aqueous Solution*. Thesis 1941, p. 198 ff. Reprinted 1957, P. Haase and Son, Copenhagen.
3. Bjerrum, J., Ballhausen, C. J. and Jørgensen, C. K. *Acta Chem. Scand.* **8** (1954) 1275.
4. Bjerrum, J. and Nielsen, E. J. *Acta Chem. Scand.* **2** (1948) 297.
5. Bjerrum, J. and Andersen, P. *Kgl. Danske Videnskab. Selskab. Mat. fys. Medd.* **22** (1945) No. 7.
6. Poulsen, I. and Bjerrum, J. *Acta Chem. Scand.* **9** (1955) 1412.
7. *Dixième Conseil de Chimie Solvay, Bruxelles 1956. Rapport et Discussions*, p. 340.
8. Stone, H. W. *Anal. Chem.* **20** (1948) 747.

Received August 14, 1957.

Acta Chem. Scand. **11** (1957) No. 8

The Preparation of Benzene-1,2,4-trisulphonic Acid

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As a part of the preliminaries for an investigation on the adsorption of benzene sulphonic acids and naphthalene sulphonic acids on aluminium oxide, asymmetrical benzene trisulphonic acid has been prepared.

After unsuccessful experiments with the method of Gattermann^{1,2}, involving the use of aniline-2,4-disulphonic acid, and after attempts to develop sulphonation products of thiophenyl derivatives, refluxing³ a solution of the sodium salt of bromobenzene-2,4-disulphonic acid⁴⁻⁷ and sodium sulphite for 6 h in the presence of some cupric sulphate turned out to be a simple and successful method.⁸ Benzene-1,4-disulphonic acid⁸ was prepared from bromobenzene-4-sulphonic acid⁹ as a preparatory study of this method.

Compared with the preparation of benzene sulphonic acid from bromobenzene, which is achieved by heating bromobenzene with a solution of sodium sulphite and cupric sulphate at 180–200°C for 7 h, the displacement of bromine from bromobenzene-2,4-disulphonic acid is clearly facilitated. As the reaction is carried out in a neutral solution, it gives some valuable information on the relative strengths of the inductive and mesomeric effects operating from the two sulphonate groups. The inductive effect (I) is opposite to the mesomeric effect (II).

I. + I effect II. — M effect

The displacement of bromine is a nucleophilic reaction:

and thus the statement is justified that the mesomeric effect of the two sulphonate groups in the bromobenzene-2,4-disulphonate ion is stronger than the corresponding inductive effect.

The common method of isolating and characterizing the sulphonic acid as the sulphonyl chloride was found not to be the proper way in this case due to the formation of chlorobenzene-2,4-disulphonyl chloride¹⁰ (m. p. 88–89°C, diamide m. p. 205–208°C) in most experiments, and so the S-benzylisothiuronium salt was chosen for this purpose. — The benzene-1,2,4-trisulphonyl chloride was prepared afterwards using mild conditions during the treatment with phosphorus pentachloride.

A convenient method of preparing bromobenzene-2,4-disulphonic acid has also been developed.

Experimental. Bromobenzene - 2,4 - disulphonic acid: A mixture of 76 g of bromobenzene and 260 ml of chlorosulphonic acid was heated at 145°C on an oil bath for 4 h with stirring. After cooling the excess of chlorosulphonic acid was carefully hydrolysed on ice. A substance insoluble in water was obtained and was thoroughly washed with 1 500 ml of ether in small portions. The volume of the ether solution was reduced to 100 ml by evaporating and after adding 200 ml of light petrol 41 g of bromobenzene-2,4-disulphonyl chloride crystallized out on cooling at 0°C (m.p. 102–104°C, diamide m.p. 241–242°C). The yield corresponds to 24 % of the theoretical amount. — The sodium salt was prepared by hydrolysing the dimethyl ester with boiling water and neutralizing with NaOH.

Benzene-1,2,4-trisulphonic acid: 25.6 g of the sodium salt of bromobenzene-2,4-disulphonic acid was refluxed for 6 h with a solution of 13.4 g (= 3 equiv.) of sodium sulphite and 1.3 g of cupric sulphate in 190 ml of water. During the reaction a red coating of Cu₂O was formed on the walls of the vessel. After cooling the solution was acidified with hydrochloric acid and air was passed through to displace the SO₂ until the odor of the gas abated. The solution was freed from precipitated CuCl by filtering, cooled in an ice bath and poured with

stirring into an ice cooled solution of 44.5 g of S-benzylisothiuronium chloride in 200 ml of water. A pale yellow precipitate was at once obtained and after a few hours' cooling on ice a white substance crystallized out. Both substances were recrystallized from 50 % alcohol and yielded 30.7 g of rectangular prisms, m. p. 240–241°C (decomp.). Another 7.5 g of the same substance was obtained from the mother liquors by evaporating and cooling.

Analysis: Found H 4.57; C 44.03; N 10.15; S 23.87. Calculated for C₆H₅[SO₃·(NH₂)₂·C·S·CH₂·C₆H₅]₃: H 4.44; C 44.11; N 10.29; S 23.55. The equivalent weight of the substance was obtained by passing it through a cation exchanger (Amberlite IR-100) and titrating with NaOH. Found 272.3, calc. 272.3. Infrared spectra showed the presence of a 1,2,4-trisubstituted benzene nucleus.

The yield of S-benzylisothiuronium benzene-1,2,4-trisulphonate, 38.2 g, was 66 % of the theoretical amount, calculated on sodium bromobenzene-2,4-disulphonate.

The sodium salt was prepared by passing a 50 % alcoholic solution of the S-benzylisothiuronium salt through a cation exchanger and neutralizing the eluate with NaOH. After evaporating the solvent the sodium salt was crystallized from 70 % alcohol and was obtained as a white powder.

Benzene-1,2,4-trisulphonyl chloride was prepared by heating the sodium salt with excess of phosphorus pentachloride at 110°C for 5 min with stirring. The reaction mixture was hydrolysed with ice water and the sulphonyl chloride was dissolved in ether and crystallized twice from light petrol; irregularly shaped crystals, m. p. 114–116°C. (Found: C 19.39. Calc. for C₆H₃(SO₂Cl)₃: C 19.29).

The writer is indebted to Professor A. Fredga and Fil. lic. G. Bendz for advice and interest.

1. Gattermann, L. *Ber.* **32** (1899) 1136.
2. Bellavita, V. *Gazz. chim. ital.* **62** (1932) 658.
3. Rosenmund, K. W. *Ber.* **54** (1921) 439.
4. Meyer, V. *Ber.* **7** (1874) 1311.
5. Fischer, P. *Ber.* **24** (1891) 3805.
6. Heinzelmann, G. *Ann.* **190** (1878) 227.
7. Zander, O. *Ann.* **198** (1879) 10.
8. Zinke, Th. and Frohneberg, W. *Ber.* **42** (1909) 2728.
9. Baxter, R. R. and Chattaway, F. D. *J. Chem. Soc.* **107** (1915) 1815.
10. Davies, W. and Wood, E. S. *J. Chem. Soc.* **1928** 1125.

Received September 17, 1957.

Acta Chem. Scand. **11** (1957) No. 8