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Abstract

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FERROCENESULFONIC ACIDS

Ferrocenesulfonic acids were obtained by us (^{1}) by the method of A. P. Terent' ev (^{2}), through the action of pyridinesulfur trioxide on ferrocene.

Simultaneously with us, ferrocenesulfonic acids were obtained by Weinmayr (^{3}) by the interaction of ferrocene with sulfuric acid in acetic anhydride and were isolated only in the form of ammonium salts.

The present work describes the sulfonation of ferrocene with pyridinesulfur trioxide and dioxanesulfur trioxide, the isolation of free mono- and disulfonic acids of ferrocene, some of their salts, methyl esters, and the acid chloride of ferrocenemonosulfonic acid.

When ferrocene is heated with pyridinesulfur trioxide in dichloroethane in a sealed tube for 4 hours, ferrocenemonosulfonic acid is obtained in 84% yield, calculated on the ferrocene that entered into the reaction; 22% of the ferrocene is isolated unchanged. With more prolonged heating of ferrocene with a larger amount of pyridinesulfur trioxide, ferrocenesulfonic acid is obtained in 41% yield together with a small amount of the monosulfonic acid. Only about 7% of ferrocene is isolated unchanged. The sulfonic acids are isolated in this case in the form of barium or lead salts.

Free ferrocenemonosulfonic acid was obtained in quantitative yield by treating the lead salt with hydrogen sulfide, and also by sulfonating ferrocene with dioxanesulfur trioxide at room temperature; the yield was 62%, calculated on the ferrocene that entered into the reaction; 54% of ferrocene is recovered unchanged.

Free ferrocenesulfonic acid was obtained by sulfonation with dioxanesulfur trioxide in dichloroethane; in this case the disulfonic acid is isolated in the form of a complex with dioxane. The yield is 85%. In sulfonation of ferrocene with sulfuric acid in acetic anhydride (^{3}), the free disulfonic acid, crystallizing with 4 molecules of water, was also isolated. The yield is 51% of theoretical. Potentiometric titration gives a curve typical for a monobasic acid, which indicates the closeness of the first and second constants and, consequently, the small influence of the sulfo groups on one another. This is an argument in favor of the location of the sulfo groups in different rings of the ferrocene molecule.

For both sulfonic acids, S-benzylthiuronium salts and salts with certain amines were obtained.

By the action of diazomethane, methyl esters of ferrocenesulfonic acids, soluble in organic solvents, were synthesized. The acid chloride of the monosulfonic acid is readily formed in good yield upon brief heating of the monoacid or its lead salt with an excess of PCl_3.

Ferrocenesulfonic acids, in contrast to aromatic sulfonic acids, are less hygroscopic and are more readily isolated in the free state. It should be noted that, for a sulfonic acid, ferrocenemonosulfonic acid has a rather low solubility in water and that its acid chloride is readily formed upon the action of PCl_3 on the free sulfonic acid, which is not typical of aromatic sulfonic acids.

Experimental Part

Ferrocenemonosulfonic Acid

To a solution of 58 g (0.312 mole) of ferrocene in 250 ml of dry dichloroethane at a temperature of 0–5°, a suspension of 55 g (0.327 mole) of dioxanesulfur trioxide in 200 ml of dichloroethane was added gradually. The mixture was left for 30 min at 0–15° and for 1.5 hours at room temperature, then treated with cold water. From the dichloroethane solution, 31.5 g (54.3%) of unreacted ferrocene was isolated. The aqueous solution was evaporated on a water bath almost to dryness. The solid residue obtained, consisting of ferrocenemonosulfonic acid, was washed with 40 ml of conc. HCl. Yield 13.5 g (62%, calculated on the ferrocene that had entered into the reaction). Ferrocenemonosulfonic acid is sparingly soluble in ether, benzene, acetone, and dioxane, somewhat better in methyl and ethyl alcohols, and rather poorly soluble in cold water. The solid sulfonic acid contains 2 molecules of water of crystallization, as shown by elemental analysis and determination of the equivalent weight by potentiometric titration; upon heating above 200° it decomposes.

Found %: C 39.56; 39.65; H 4.38; 4.55; Fe 18.70; 18.50
$C_{10}H_{14}O_5SFe$. Calculated %: C 39.75; H 4.68; Fe 18.49

Found equiv. wt. 303; 309; for $C_{10}H_{14}O_5SFe$ calculated: equiv. wt. 302.

Free ferrocenemonosulfonic acid was also obtained by treating the lead salt with hydrogen sulfide.

4 g of the lead salt were dissolved in 150 ml of water; the lead was precipitated by passing in hydrogen sulfide. The precipitated PbS was separated by centrifugation. The water was removed in vacuo in a stream of CO_2. The ferrocenemonosulfonic acid was dried in a vacuum desiccator over P_2O_5. Yield 1.5 g (97% of theory).

Ferrocenemonosulfonic acid isolated from the lead salt and obtained by sulfonation of ferrocene with dioxanesulfur trioxide gives one and the same acid chloride.

Lead salt. The reaction mixture after sulfonation of ferrocene with dioxanesulfur trioxide (the conditions were the same as described in the preceding experiment) was treated, with heating, with 70 g of $PbCO_3$. This gave 45 g (80%, calculated on the ferrocene that had entered into the reaction) of the lead salt of ferrocenemonosulfonic acid, crystallizing from hot water with $3H_2O$.

Found %: C 30.10; 30.28; H 3.00; 3.05

$C_{20}H_{26}O_9S_2Fe_2Pb$. Calculated %: C 30.34; H 3.06

Barium salt. A mixture of 12 g (0.065 mole) of ferrocene, 40 g (0.25 mole) of pyridinesulfur trioxide, and 20 ml of dry dichloroethane was heated for 4 hours in a sealed tube on a boiling water bath. After treatment of the reaction mixture with water and $BaCO_3$, 2.7 g (22.4%) of unreacted ferrocene and 15.6 g (84%, calculated on the ferrocene that had entered into the reaction) of the barium salt of ferrocenemonosulfonic acid were isolated; this salt is insoluble in organic solvents, rather difficultly soluble in cold water and readily soluble in hot water; it crystallizes from water as a crystalline hydrate with $3H_2O$.

Found %: C 33.28; 33.21; H 3.44; 3.39

$C_{20}H_{24}O_9S_2Fe_2Ba$. Calculated %: C 33.16; H 3.34

S-Benzylthiuronium salt was obtained by mixing equimolecular amounts of aqueous solutions of the barium salt of ferrocenemonosulfonic acid and S-benzylthiuronium chloride, m.p. 220-222° (from 50% alcohol).

Found %: C 50.04; 49.91; H 4.69; 4.70

$C_{18}H_{20}O_3N_2S_2Fe$. Calculated %: C 50.00; H 4.66

The free ferrocenemonosulfonic acid forms with chlorinated *S*-benzylthiuronium a salt identical with that obtained from the barium salt.

Salts with amines. With aromatic and aliphatic amines, ferrocenemonosulfonic acid readily gives salts that are readily soluble in water and decompose in air. A salt with diethylamine is formed excellently on adding an excess of the amine to the sulfonic acid, m.p. 118-120°.

Found, %: C 49.45; 49.52; H 6.30; 6.21; Fe 16.67; 16.60; N 4.61; 4.91

$C_{14}H_{21}O_3NSFe$. Calculated, %: C 49.56; H 6.24; Fe 16.46; N 4.13

Methyl ester. A suspension of 3 g of ferrocenemonosulfonic acid in 20 ml of ether was treated with an ethereal solution of diazomethane obtained from 10.3 g of nitrosomethylurea. Yield 2 g (72% of theory), m.p. 52-54° (from ether on cooling to 0°).

Found, %: C 47.48; 47.39; H 4.46; 4.38; Fe 20.06; 20.05
$C_{11}H_{12}O_3SFe$. Calculated, %: C 47.16; H 4.32; Fe 19.93

Acid chloride. 3 g of ferrocenemonosulfonic acid was added in small portions to 30 ml of PCl_3. The mixture was heated for 30 min on a water bath. The resulting solution was filtered from a small insoluble residue, which was treated once more with 10 ml of PCl_3. The solutions were combined, and part of the PCl_3 (25 ml) was distilled off. On cooling, 0.7 g of dark-orange crystals of the acid chloride separated. To the solution, 25 ml of cold water was cautiously added, and a further 1.05 g of the acid chloride separated. The total yield was 1.75 g (62% of theory).

The acid chloride is readily soluble in organic solvents and is slowly hydrolyzed on standing in air with formation of the original sulfonic acid; m.p. 72-73° in an open capillary and 77-78° in a sealed one (from a mixture of hexane and benzene, 5:1).

Found, %: C 41.89; 41.68; H 3.47; 3.60; Fe 19.70; 19.61
$C_{10}H_9O_2SClFe$. Calculated, %: C 42.21; H 3.19; Fe 19.63

The acid chloride was also obtained in good yield by analogous treatment of the lead salt of ferrocenemonosulfonic acid.

Ferrocenendisulfonic Acid

To a suspension of 10.7 g (0.0575 mole) of ferrocene in 10 ml of dichloroethane was added a suspension of 29 g (0.172 mole) of dioxanesulfur trioxide in 50 ml of dichloroethane at a temperature of −20 to −30°. The mixture was left overnight at room temperature. The precipitated pure ferrocenendisulfonic acid was filtered off, washed with dioxane and dichloroethane, and dried in a vacuum desiccator for 24 hours; it contains one molecule of crystallization dioxane. Yield 21.1 g (85% of theory).

Found, %: C 38.26; 38.18; H 4.40; 4.42; Fe 13.12; 13.18
$C_{14}H_{18}O_8S_2Fe$. Calculated, %: C 38.71; H 4.18; Fe 12.86

On standing in a vacuum desiccator, ferrocenendisulfonic acid readily loses the molecule of crystallization dioxane, turning into the anhydrous disulfonic acid, which rapidly absorbs moisture from the air.

Free ferrocenendisulfonic acid was also isolated by us in the sulfonation of ferrocene with sulfuric acid in acetic anhydride (^{3}).

To a solution of 9.3 g (0.05 mole) of ferrocene in 150 ml of acetic anhydride was gradually added 10 ml (0.188 mole) of conc. sulfuric acid while cooling to 0, +5°. The mixture was left for 12 hours at 0°. The precipitated ferrocenendisulfonic acid was filtered off, washed with a small amount of acetic anhydride, and then thoroughly washed with benzene. Yield 10.8 g (51% of theory). M.p. 80-90°; it could not be recrystallized.

The ferrocenendisulfonic acid obtained by the method described above contains 4 molecules of water of crystallization, as shown by analysis.

and determination of the equivalent weight by potentiometric titration; on standing in air, the thoroughly washed acid absorbs moisture rather slowly.

Found, %: C 29.23; 29.09; H 4.58; 4.48; Fe 12.5; 12.1
$C_{10}H_{18}O_{10}S_2Fe$. Calculated, %: C 28.72; H 4.32; Fe 13.6

A purer ferrocenedisulfonic acid is obtained if the product described above is extracted for a long time with benzene in a Soxhlet apparatus. After partial distillation of the benzene, golden-yellow crystals separate, identical in properties with those described above, giving the same dimethyl ester and still containing 4 molecules of water of crystallization*.

Found, %: C 28.71; 28.59; H 4.08; 4.29; Fe 13.31; 13.70
$C_{10}H_{18}O_{10}S_2Fe$. Calculated, %: C 28.72; H 4.32; Fe 13.36

Found equiv. wt. 203; 203; for $C_{10}H_{18}O_{10}S_2Fe$ the calculated equiv. wt. is 209.

Barium salt. 10 g (0.054 mole) of ferrocene, 40 g (0.25 mole) of pyridinesulfur trioxide, and 20 ml of dichloroethane were heated in a sealed tube on a boiling water bath for 8 hours. After treatment of the reaction mixture with water and $BaCO_3$, 11.5 g (41%, based on the reacted ferrocene) of the barium salt of ferrocenedisulfonic acid was isolated; 0.7 g (7%) of ferrocene was recovered unchanged. The barium salt dissolves very well in water, is precipitated from a saturated aqueous solution by alcohol, and is freed from admixture of the barium salt of the monoacid by repeated reprecipitation.

Found, %: C 21.19; 21.22; H 2.79; 2.74
$C_{10}H_{16}O_{10}S_2FeBa$. Calculated, %: C 21.69; H 2.91

S-Benzylthiuronium salt was obtained in the same way as for the monoacid, m.p. 233–235° (from 50% alcohol or from water).

Found, %: C 46.08; 46.22; H 4.74; 4.71
$C_{24}H_{30}O_6N_4S_4Fe$. Calculated, %: C 46.01; H 4.46

Salts with amines. Ferrocenedisulfonic acid readily forms salts with amines under the action of an excess of amine. The salt with dimethylaniline does not melt on heating to 250°**.

Found, %: C 52.82; 52.65; H 5.52; 5.61; Fe 10.50; 10.82
$C_{26}H_{32}N_2S_2O_6Fe$. Calculated, %: C 53.09; H 5.48; Fe 10.88

Dimethyl ester. To a mixture of 0.65 g of the tetrahydrate of ferrocenedisulfonic acid in 20 ml of ether, an ethereal solution of diazomethane prepared from 5.2 g of nitrosomethylurea was added with ice cooling. Yield 95% of theory. M.p. 140–142°. The ester is almost insoluble in cold methyl and ethyl alcohols, in acetic acid and in water; sparingly soluble in ether and benzene; better soluble in acetone, pyridine, dichloroethane, and dioxane.

Found, %: C 38.83; 38.72; H 4.19; 4.18; Fe 15.01; 14.95
$C_{12}H_{14}O_6S_2Fe$. Calculated, %: C 38.50; H 3.77; Fe 14.93

Ferrocenedisulfonic acids obtained by different methods give the same dimethyl ester.

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* Obtained jointly with S. P. Gubin.
** Obtained by S. P. Gubin.

Note: Figure translations are in progress. See original paper for figures.