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## Abstract

## Full Text

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# FERROCENESULFINIC ACIDS

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Earlier ($^1$) we described the preparation of sulfinic acid by reduction of ferrocenesulfochloride with zinc dust. In the present work we have synthesized ferrocenedi-sulfinic acid and studied the properties of both acids.

Ferrocenedi-sulfinic acid was obtained by reduction of the acid chloride of ferrocenedi-sulfonic acid with zinc dust. It is poorly soluble in water and in organic solvents; its solutions decompose rapidly. The disodium salt of ferrocenedi-sulfinic acid is considerably more stable.

Ferrocenesulfinic acids, both the mono- and the diacid, react with sublimate similarly to benzenesulfinic acid, giving mono- and di(chloromercury)ferrocenes in high yield

$$C_5H_5FeC_5H_4SO_2Na \xrightarrow{HgCl_2} C_5H_5FeC_5H_4HgCl,$$

$$Fe(C_5H_4SO_2Na)_2 \xrightarrow{HgCl_2} Fe(C_5H_4HgCl)_2.$$

We attempted, in an analogous manner, by the action of stannous chloride on the sodium salt of the sulfinic acid, to obtain an organotin derivative of ferrocene, but it turned out that reduction takes place and tin dithioferrocenolate is formed

$$2C_5H_5FeC_5H_4SO_2Na \xrightarrow{SnCl_2} (C_5H_5FeC_5H_4S)_2Sn.$$

Tin thioferrocenolate was identified by converting it into thioferrocenyl benzoate.

Next we used ferrocenemonosulfinic acid for the synthesis of ferrocenyl sulfones.

Earlier ($^2$) we obtained phenyl ferrocenyl sulfone and diferrocenyl sulfone by the action of the acid halides of the corresponding sulfonic acids on diferrocenylmercury. In the present work we synthesized benzyl-, triphenylmethyl-, and picrylferrocenyl sulfones by the interaction of the sodium salt of ferrocenemonosulfinic acid with benzyl chloride, triphenylchloromethane, and picryl chloride, respectively:

$$C_5H_5FeC_5H_4SO_2Na \begin{cases} \xrightarrow{C_6H_5CH_2Cl} C_5H_5FeC_5H_4SO_2CH_2C_6H_5, \\ \xrightarrow{(C_6H_5)_3CCl} C_5H_5FeC_5H_4SO_2C(C_6H_5)_3, \\ \xrightarrow{(NO_2)_3C_6H_2Cl} C_5H_5FeC_5H_4SO_2C_6H_2(NO_2)_3. \end{cases}$$

The yields are high (80–88% of theory).

Ferrocenyl(ferrocenylmethyl) sulfone was obtained in good yield by heating an aqueous solution of the sodium salt of ferrocenesulfini-

acid with iodomethylate of (N,N-dimethylaminomethyl)ferrocene

$$C_5H_5FeC_5H_4SO_2Na + J(CH_3)_3NCH_2C_5H_4FeC_5H_5 \rightarrow$$

$$\rightarrow C_5H_5FeC_5H_4SO_2CH_2C_5H_4FeC_5H_5 + NaJ + N(CH_3)_3.$$

## Experimental Part

**Reaction of the sodium salt of ferrocenesulfinic acid with mercuric chloride.** To an aqueous solution of 0.31 g (0.001 mole) of the sodium salt of ferrocenesulfinic acid was added an alcoholic solution of 0.27 g (0.001 mole) of mercuric chloride. A precipitate of chloromercuriferrocene immediately separated ($^3$), which was filtered off and dried. Weight 0.41 g. Yield quantitative. M.p. and mixed m.p. with chloromercuriferrocene 194–196°.

**Tin thioferrocenolate.** To a suspension of 0.37 g (0.0012 mole) of the sodium salt of sulfinic acid in alcohol was added 0.5 g of stannous chloride. The pale-yellow precipitate that separated in the cold was converted on heating into a red crystalline substance—tin thioferrocenolate. Weight 0.2 g (yield 74% of theoretical). Tin thioferrocenolate is readily soluble in benzene, less soluble in ether, insoluble in petroleum ether and *n*-heptane; it was purified by precipitation with petroleum ether from a benzene solution.

| | |
|---|---|
| Found, %: | C 43.68; 43.59; H 3.34; 3.37 |
| $C_{20}H_{18}FeS_2Sn$. Calculated, %: | C 43.42; H 3.25 |

On treatment of tin thioferrocenolate with hydrochloric acid, ferrocenyl mercaptan was obtained, which was isolated in the form of the benzoyl derivative. M.p. and mixed m.p. with an authentic sample 138–139°.

**Triphenylmethyl ferrocenyl sulfone.** A suspension in ether of 0.55 g (0.0018 mole) of the sodium salt of ferrocenylsulfinic acid and 0.5 g (0.0018 mole) of triphenylchloromethane was heated for 4 hr. The precipitated triphenylferrocenyl sulfone was recrystallized from *n*-butyl alcohol. Triphenylmethyl ferrocenyl sulfone is a yellow crystalline substance, sparingly soluble in organic solvents; it melts with decomposition at 220–221°.

Found, %: C 70.09; 70.14; H 5.07; 5.04; S 6.35; 6.24; Fe 11.54; 11.32
$C_{29}H_{24}FeO_2S$. Calculated, %: C 70.61; H 4.91; S 6.48; Fe 11.38

**Benzyl ferrocenyl sulfone.** An alcoholic solution of 0.55 g (0.0018 mole) of the sodium salt of ferrocenylsulfinic acid and 0.5 g of benzyl chloride was heated for 4 hr to boiling. Then the solvent was distilled off, and the residue was extracted with benzene. The benzene extracts were chromatographed on a column of alumina. Benzyl ferrocenyl sulfone was eluted with benzene. After recrystallization from alcohol, m.p. 144–146°. Yield 0.4 g (80% of theoretical).

Found, %: C 59.88; 60.01; H 4.87; 4.84; Fe 16.20; 15.98
$C_{17}H_{16}FeO_2S$. Calculated, %: C 60.01; H 4.73; Fe 16.46

**Picryl ferrocenyl sulfone.** A mixture of 0.55 g (0.0018 mole) of the sodium salt of ferrocenesulfinic acid and 0.87 g (0.0035 mole) of picryl chloride was heated in alcohol for one hour. The picryl ferrocenyl sulfone, which separated as a dark-violet crystalline precipitate, was purified by three reprecipitations from benzene with *n*-heptane; it contains 0.5 molecule of benzene of crystallization. Picryl ferrocenyl sulfone is readily soluble in benzene, sparingly soluble in ethyl and butyl alcohols, insoluble in ether and petroleum ether; it does not melt, and explodes on combustion. Yield 88% of theoretical.

Found, %: C 45.37; 45.39; H 2.87; 3.15; S 6.37; 6.17; Fe 11.46; 11.68
$C_{19}H_{14}FeO_8SN_3$. Calculated, %: C 45.59; H 2.82; S 6.41; Fe 11.16

**Ferrocenyl(ferrocenylmethyl)sulfone*.** A solution of 1.4 g (0.0036 mole) of iodomethylate of (N,N-dimethylaminomethyl)ferrocene (4) in 150 ml of water was added to a solution of 1 g (0.0032 mole) of the sodium salt of ferrocenesulfinic acid in 70 ml of water. The mixture was heated for 3 hr at 80–90° and then for 2 hr to boiling. The yellow precipitate of sulfone that separated was filtered off, thoroughly washed with water, and dried in a vacuum desiccator. Weight 1.35 g. From the filtrate, after acidification with conc. HCl, a further 0.15 g of sulfone was isolated. Total yield 1.5 g (92% of theory). M.p. above 175–180° after reprecipitation with *n*-heptane from benzene solution.

Found, %: C 55.98; 56.19; H 4.55; 4.41; Fe 24.36; 24.25; S 6.95; 7.18
$C_{21}H_{20}FeSO_2$. Calculated, %: C 56.30; H 4.47; Fe 24.94; S 7.40

**Dichloroanhydride of ferrocenedisulfonic acid**.** To 100 ml of $POCl_3$ there was added, in small portions, 32 g (0.074 mole) of the complex of ferrocenedisulfonic acid with dioxane (5). The mixture was heated on a water bath for 40 min, then cooled and poured onto ice. The precipitate was filtered off and extracted several times with hot dichloroethane. The solution of the dichloroanhydride of the disulfonic acid in dichloroethane was dried with magnesium sulfate. The dichloroethane was distilled off until crystallization began. The dichloroanhydride of ferrocenedisulfonic acid that separated on cooling to 0° was filtered off and washed with dichloroethane. Weight 15 g. From the mother liquor a further 2 g of dichloroanhydride was isolated. Total yield 17 g (60% of theory). The dichloroanhydride of ferrocenedisulfonic acid was recrystallized from a (1:1) mixture of dichloroethane and $CCl_4$; on heating above 150° it decomposes vigorously.

**Ferrocenedisulfinic acid and its sodium salt.** A saturated benzene solution of 6 g (0.0145 mole) of the dichloroanhydride of ferrocenedisulfonic acid was heated with 10 g of zinc dust and 1 ml of water for 3-4 hr (until the benzene solution was completely decolorized). During heating, fresh portions of zinc dust (2 g each) and water (0.5 ml each) were added three times. The precipitate was then filtered off and treated, with heating, with four portions (150 ml each) of a cold-saturated soda solution. The alkaline solution, carefully cooled with ice water in order to avoid decomposition of ferrocenedisulfinic acid, was acidified with conc. HCl. A flocculent precipitate of ferrocenedisulfinic acid formed. Weight 2.75 g. Yield 56% of theory***. Ferrocenedisulfinic acid is a yellow powdery substance with m.p. 126–128°, poorly soluble in water and in organic solvents. On heating its solutions, rapid decomposition occurs. The sodium salt of ferrocenedisulfinic acid was obtained by precipitation with 40% alkali from alcoholic or aqueous weakly alkaline solutions, and also directly from a soda solution of its sodium salt. After recrystallization from alcohol, the sodium salt of the disulfinic acid is a yellow crystalline substance, readily soluble in water, methyl and ethyl alcohols; on heating it decomposes without melting at 290–298°; it contains 3 molecules of water of crystallization.

Found, %: C 28.97; 28.90; H 3.75; 3.64; S 14.82; 14.92
$C_{10}H_{14}FeO_7S_2Na_2$. Calculated, %: C 29.1; H 3.42; S 15.35

* Ferrocenyl(ferrocenylmethyl)sulfone was obtained jointly with L. S. Shilovtseva and A. A. Ponomarenko.

** Previously (1) we described the preparation of the dichloroanhydride of ferrocenedisulfonic acid from the lead salt of the disulfonic acid. In the present work we found that the dichloroanhydride is readily obtained from the complex of ferrocenedisulfonic acid with dioxane, which makes preparation of the lead salt unnecessary.

*** In obtaining ferrocenedisulfinic acid there is some subtlety that has not been clarified by us, since at times it was not possible to isolate it by acidifying the soda solution with conc. HCl, despite careful observance of the conditions of successful experiments.

**Reaction of the sodium salt of ferrocenedisulfinic acid with sulema.** On heating an alcoholic solution of 0.32 g (0.0078 mole) of the sodium salt of ferrocenedisulfinic acid and 0.55 g (0.002 mole) of sulema, ferrocenediyl(mercury chloride) ($^3$) was formed (isolated as a yellow precipitate). Yield 0.41 g (80% of theoretical).

Found, %: C 18.64; 18.57 H 1.49; 1.36
$C_{10}H_8FeHg_2Cl_2$. Calculated, %: C 18.32; H 1.23

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

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