ACTA CHEMICA SCANDINAVICA 17 (1963) 377–382

Studies on Sulfinic Acids

I. Preparation and Purification of Aromatic Sodium Sulfinates

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In connection with a kinetic study, a series of aromatic sodium sulfinates was needed. As isolation and purification of the sulfinic acids is inconvenient because of their tendency to disproportionation, suitable, practical methods for their isolation as salts were investigated and applied for the preparation of the sodium salts. These have been purified and analyzed.

Methods for preparation of aromatic sulfinic acids are well represented in chemical literature [1,2], and the raw material for the preparation of the salts described in this paper was produced by well-known methods or their modifications.

Reduction of sulfonyl chlorides to the corresponding sulfinic acids has been used, under various conditions, by different authors, and this method was employed here for sulfonyl chlorides which were commercially available or could be easily synthetized. Hydrolysis of sulfenyl chloride [3–7] was used in one case. Substitution of the diazonium group, according to Gattermann [8] as modified by Lange [9] for application to negative substituents, was used when suitable aromatic amines were commercially available. Appropriate references, and observations on these methods are given in the experimental part.

The arylsulfinic acids are sparingly soluble in water at room temperature. Some are reported to withstand recrystallization from water or other solvents, but it is inadvisable to purify them as acids, because of the tendency to disproportionation. Moreover, as the sodium salts were required, isolation and purification were focussed on purifying the salts. They often have a suitable solubility in organic solvents or water-organic solvent mixtures for recrystallization. All the *para*-substituted and the nitro-substituted sulfinates have excellent crystallization properties. Repeated recrystallizations did not always prove sufficient. In such cases the acid was reprecipitated with sulfuric

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acid and neutralized. Hydrochloric acid was avoided because of its catalytic effect on the decomposition of sulfinic acids[10,11], and also because it was desirable, for other reasons, to keep at a minimum the risk of halide impurity.

Sulfinates can be isolated also as insoluble salts, and among others, the ferric salt has been both recommended[12], and used to some extent[13-15]. The precipitates, however, are very difficult to filtrate. Isolation as the zinc salt, which is decomposed by sodium carbonate, was more convenient, and was used in some cases.

By extraction or dissolution of reprecipitated sulfinic acid in a suitable organic solvent and neutralization with alkali alcoholate, the alkali salt can be precipitated quantitatively. This method was applied, when the salt was too soluble in water mixtures, in order to avoid evaporation and the accompanying risk of oxidation.

The purification operations were followed by titration and were repeated to constant equivalent weight or as many times as yields permitted.

Titration with potassium permanganate in neutral solution, and with perchloric acid in glacial acetic acid solution, was generally applicable for the determination of equivalent weights of the pure salts. The reaction of sulfinic acids with nitrous acid can be used as a specific titration method for determining the sulfinate content[16] but it was not completely quantitative, and all sulfinates were not satisfactorily reactive.

$$2\ RSO_2H + HNO_2 \longrightarrow (RSO_2)_2NOH + H_2O$$

The titrimetric methods for the determination of the sulfinic acid or sulfinate group will be described in detail in a later paper.

The sodium sulfinates crystallize with crystal water or crystal alcohol. Although they easily lose their crystal solvent in the air, in some cases it is difficult to remove the last traces of crystal solvent. Consequently, the salts must be carefully dried at elevated temperature and reduced pressure before analysis. Thus dried, some salts are hygroscopic. These facts account for a tendency to high hydrogen values in the elementary analysis.

The analytical data on the purified dried salts are shown in Table 1. Some of the sulfinates were stored for a protracted period in ordinary, stoppered bottles in air at room temperature and proved to be satisfactorily stable.

EXPERIMENTAL

Reduction of sulfonyl chloride. Sodium sulfite was used as a reducing agent according to Krishna and Singh[17]. The reaction solution was kept neutral by means of a pH stat during reaction and the sulfinic acid was precipitated by sulfuric acid. Excess sulfite, which was often used by previous workers, proved unnecessary. Increased temperature, according to Bredereck *et al.*[18] was applied with success, and the reductions were usually carried out at about 80°.

p-Toluenesulfinate. For purification, the acid was reprecipitated from the salt and neutralized. The salt was isolated by partial evaporation[19] and recrystallized four times from water-ethanol.

Benzenesulfinate. Ether extraction of the sulfinic acid and extraction of the ether solution with sodium hydroxide solution gave, after recrystallization, a good yield of sodium sulfinate. Reprecipitation as acid, and neutralization. Recrystallized once from water-ethanol and once from ethanol.

Table 1. Analyses of aromatic sodium sulfinates.

Sulfinate	Titrimetric equivalent weight [a]				Elementary analysis			
	$E_{\text{Calc.}}$	E_{KMnO_4}	E_{HClO_4}	E_{HNO_3}	C Found/Calc.	H Found/Calc.	S Found/Calc.	X Found/Calc.
$C_6H_5SO_2Na$	164.1	164.0	164.0	167.1	43.9 (44.1)	3.3 (3.05)	19.7 (19.5)	
		165.2	165.1					
o-$CH_3C_6H_4SO_2Na$	178.2	180.3 179.7	179.7	Slow, unsharp	47.1 (47.1)	4.0 (3.93)	17.8 (17.9)	
m-		178.4	178.0	Unsharp	47.2	3.8	17.8	
		179.0	178.5					
p-		178.8	179.3 179.2	180.5	47.0	4.1	17.6	
o-$CH_3OC_6H_4SO_2Na$	194.2	199.5	198.3 199.4	No reaction	42.8 (43.3)	3.8 (3.64)	16.2 (16.5)	
m-		198.2	201.8	201.8	43.2	3.7	16.2	
			201.2					
p-		—	196.0	200.8	43.2	3.8	16.3	
			197.0					
o-$ClC_6H_4SO_2Na$	198.6	199.1 199.2	201.0 201.3	No reaction	36.1 (36.3)	2.1 (2.02)	16.0 (16.1)	17.8 (17.9)[b]
m-		199.5 199.1	197.8 197.8	200.0	36.3	1.9	16.0	17.8
p-		198.6	199.8 200.4	201.4	36.3	2.0	16.2	17.8
o-$NO_2C_6H_4SO_2Na$	209.1	209.4 209.3	209.6 209.7	No reaction	34.3 (34.4)	2.0 (1.91)	15.5 (15.3)	6.89 (6.70)[c]
m-		210.0	209.1 210.0	Slow, unsharp	34.3	2.1	15.3	6.72
p-		209.7	209.4 210.5	Slow	34.6	2.1	15.4	6.77

a) Double titrations are represented horisontally and different samples vertically.
b) X = Cl
c) X = N

p-Methoxybenzenesulfonyl chloride was prepared according to Morgan *et al.*[13]

p-Methoxybenzenesulfinate. The dispersion of the sulfonyl chloride was facilitated by adding a few drops of detergent. The main bulk of sulfinate crystallized from the reaction mixture when cooling, and the rest was isolated by acidification. Reprecipitation as acid. Neutralization in ether with sodium hydroxide in ethanol. Four consecutive recrystallizations from water, ethanol water 10:3, dioxane-ethanol-water 9:3:4, and water, did not yield a pure product. The sulfinate was therefore further purified *via* the ferric salt and treated with an ion exchanger according to Overberger and Godfrey [15]. The sodium salt was isolated by the precipitation of the acid, which was dissolved in acetone, neutralized by methanolic sodium hydroxide and precipitated by ether. The best analyses were obtained after two recrystallizations from water. Repeated recrystallization resulted in decomposition of the salt. This sulfinate is very reactive and cannot be titrated by permanganate. Even under the mildest conditions the aromatic nucleus is oxidized by permanganate.

p-Chlorobenzenesulfonyl chloride was prepared according to Muth [20].

p-Chlorobenzenesulfinate was prepared according to Muth [20]. Reprecipitated as acid, and neutralized. Recrystallized three times: once from water, once from ethanol, and finally, from ethanol-water 1:1.

o-Nitrobenzenesulfonyl chloride was prepared according to Wertheim [21] by oxidating chlorination of *o,o'*-dinitrodiphenyldisulfide with nitric acid as oxidant.

o,o'-Dinitrodiphenyldisulfide was prepared according to Wolhfahrt [22].

o-Nitrobenzenesulfinate was prepared according to Zincke and Farr [3]. Isolation by sulfinic acid-ether extraction, and the subsequent extraction of this solution by sodium hydroxide, gave the sulfinate as dihydrate. Reprecipitated as acid and neutralized. Recrystallized twice from ethanol and once from ethanol-water.

m-Nitrobenzenesulfonyl chloride was prepared according to Hodgson and Whitehurst [23].

m-Nitrobenzenesulfinate. Reduction at 100°. Isolation by ether extraction of the acid and soda neutralization gave the sulfinate as dihydrate. Recrystallized twice from ethanol and once from ethanol-water.

Hydrolysis of sulfenyl chloride. o-Nitrobenzenesulfenyl chloride was prepared according to Hubacher [24] by treating *o,o'*-dinitrodiphenyldisulfide with chlorine.

o-Nitrobenzenesulfinic acid was prepared according to Zincke and Farr [3] by treating *o*-nitrobenzenesulfenyl chloride with 2 N sodium hydroxide. Sulfinic acid was obtained from the mother liquor by acidification and extraction.

Substitution of the diazonium group. The substitution of the diazonium group was effected by the method of Lange [9] with slight modifications necessitated by the enlargement of the scale 10 times.

The redistilled or recrystallized amine is diazotized in a mixture of sulfuric and phosphoric acids, with 20 % excess sodium nitrite, whereafter the excess is decomposed by aminosulfonic acid. The diazonium salt solution is then saturated with excess sulfur dioxide under ice-cooling. Rapid operation is a necessary condition for good yields. Consequently, the saturation time was reduced by introducing the sulfur dioxide under slight pressure and by using two gas inlets. The solution is mixed with finely powdered ferrous sulfate heptahydrate and freshly prepared copper powder. The mixture is stirred, and the reaction that is accompanied by nitrogen evolution is carried out at a suitable temperature, depending on the rate of reaction. Isolation is effected by filtering off the precipitate obtained, which contains sulfinic acid and thiosulfonate. The filter cake was extracted by vigorous shaking with a suitable solvent, followed by filtration. If the sulfinic acid did not precipitate quantitatively (in strong acid solution the solubility of sulfinic acids increase), then the reaction mixture was also extracted after subjection to suction, in order to remove excess sulfur dioxide. Because of the instability of sulfinic acids, evaporation of the extract cannot be recommended, especially with regard to larger quantities; and hence, the sulfinate was precipitated directly from the extract by ammonia gas under ice-cooling. The ammonium salt precipitates completely and evaporation is prevented. The extract need not be dried; the content of some water actually facilitates crystallization, as the ammonium salts crystallize with crystal water.

The following sulfinates were prepared in this way.

o-Toluenesulfinate. The reaction mixture was extracted and the ammonium salt was precipitated. From this salt the acid was reprecipitated, taken up in ether, and the ether solution then neutralized with sodium hydroxide in methanol. A large volume of ether was required to precipitate the main bulk of the salt. The sodium salt was recrystallized three times from dioxane mixed with a small amount of ethanol and a fourth time from dioxane mixed with a small amount of water.

m-Toluenesulfinate. The sulfinic acid separated as an oil. The ether-methylene chloride extract was deeply coloured and could be partly decolorized by activated carbon. The ammonium salt contained an impurity that could be removed by ether extraction. The salt had very inferior crystallization properties. It could not be crystallized by neutralizing an ether solution of the sulfinic acid with sodium hydroxide. Therefore, the zinc salt was precipitated from the ammonium salt. Washing with ethanol-ether-acetone removed accompanying impurities. The zinc sulfinate was extracted with soda solution. The extract was concentrated and the acid reprecipitated. After this procedure, it was possible to bring the salt to crystallization by neutralizing the ether solution of the acid with sodium hydroxide in ethanol. Recrystallized three times from dioxane.

o-Methoxybenzenesulfinate. Extraction with ether and decolorization with carbon. Reprecipitated as acid. The acid was recrystallized from chloroform. Neutralization in ether-methylene chloride with sodium hydroxide in ethanol. Recrystallization twice from ethanol and some water. The water was necessary to facilitate crystallization.

m-Methoxybenzenesulfinate. The reaction mixture became very dark during diazotization and evolved nitrous gases. Extraction with ether gave very impure ammonium salt, which was extracted with acetone and reprecipitated as zinc sulfinate. The zinc sulfinate was treated with excess sulfuric acid and extracted with ether. The ether solution was neutralized with sodium hydroxide in ethanol. The sodium salt was very soluble and had inferior crystallization properties. Recrystallized once from ethanol-ether, once from dioxane-ether, and finally from a small amount of water. The yield did not permit further purification.

o-Chlorobenzenesulfinate. Extraction with ether. The acid was precipitated from the ammonium salt and was recrystallized twice from chloroform. (E_{KMnO_4} 177.2; E_{NaOH} 176.6; E_{TBAH} 177.3; $E_{Calc.}$ 176.6. Found: C 40.4; H 2.9. Calc. for $C_6H_5O_2SCl$; C 40.8; H 2.9). The salt was precipitated from chloroform with sodium methoxide and recrystallized from ethanol.

m-Chlorobenzenesulfinate. Extraction with ether. Purified in the same way as the *m*-toluenesulfinate *via* the zinc salt. Recrystallized twice from ethanol.

p-Nitrobenzenesulfinate. The reaction took place with excessive foaming. The sulfinic acid had a low solubility in organic solvents and was extracted with acetone-chloroform. Reprecipitated as acid and neutralized. Recrystallized twice from ethanol.

Stability of sodium sulfinates. Some of the sulfinates were stored as crystals with crystal solvent, except the *p*-toluenesulfinate, which was stored in the dried form as a fine powder. No significant change in the equivalent weight of the dried salts could be detected, except for the *p*-toluenesulfinate. Benzenesulfinate: E_{KMnO_4} 163.9, after 3 years and 9 months 164.1. E_{HNO_2} 166.2, after 3 years and 9 months 167.6.
p-Toluenesulfinate: E_{HNO_2} 179.7, after 4 years and 3 months 187.0.
o-Chlorobenzenesulfinate: E_{KMNO_4} 200.3, after 1 year 199.1.
m-Nitrobenzenesulfinate: E_{KMnO_4} 210.1, after 2 years 210.5.

Acknowledgements. The author wishes to express his gratitude to Professor Erik Larsson for his interest in this work. Grants from the *Kungliga Fysiografiska Sällskapet* and the *Matematisknaturvetenskapliga Fakulteten,* University of Lund, are gratefully acknowledged.

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Received September 3, 1962.