PAPER CHROMATOGRAPHY OF SULFINIC ACIDS AND THEIR DETECTION

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A method of detection of aromatic sulfinic acids has been proposed, based on the treatment with nitrous gases, followed by spraying with a solution of the sodium salt of 2-naphthol-3,6-disulfonic acid (R-salt) and exposure to ammonia vapours. The mechanism of this method of detection has been elucidated. Chromatographic analysis of four aromatic sulfinic acids in several solvent systems has also been carried out.

Paper chromatography of sulfinic acids or sulfonyl chlorides was investigated by Gringras and Sjoestedt[1] who detected them with tetrazotized *o*-dianisidine in the form of a salt stabilized with zinc chloride (Echtblau B Salz, E. Merck); with this reagent sulfinic acids give canary-yellow spots. They used the ascending technique in the solvent system 1-butanol–1-propanol–water (1 : 1 : 1).

When chromatographing the reaction mixture after reduction of *m*-nitrobenzenesulfonyl chloride with sodium sulfite[2] in 1-propanol–ammonia (2 : 1) and carrying out the detection with nitrous gases and spraying with a solution of R-salt and exposing to ammonia vapours a clear yellow-green spot appeared on the chromatograms in addition to orange-red spots of aminobenzenesulfonic acids (which give orange-red azo-dyes). From the colour of the former spot and from its position (maximum value R_F 0·79) it was evident that this detection was not based on the azo-coupling reaction and that the detected substance was not diazotizable.

During the reduction of *m*-nitrobenzenesulfonyl chloride *m*-nitrobenzenesulfinic acid[2] is also formed. A parallel chromatogram of the solution after reduction and an authentic sample proved that the yellow-green spot does correspond to *m*-nitrobenzenesulfinic acid.

The chemistry of the observed detection could be elucidated and confirmed in the following manner: sulfinic acid reacts with nitrous gases under formation of corresponding N,N-diarylsulfonyl-hydroxylamine

$$(RSO_2)_2NOH$$

$$I\ (\text{ref.}^3),\ R = C_6H_5; \qquad II\ (\text{ref.}^{4,5}),\ R = p\text{-}H_3C.C_6H_4;$$

$$III,\ R = p\text{-}H_3CCONH.C_6H_4; \qquad IV,\ R = m\text{-}O_2N.C_6H_4$$

in the same manner as with nitrous acid[3–5]. After spraying with a solution of R-salt and exposure to ammonia gas N,N-diarylsulfonyl-hydroxylamine is hydrolysed first under liberation of nitrous acid (in alkaline medium N,N-diarylsulfonyl-hydroxylamines are hydrolysed to sulfinic acids and HNO_2 (ref.[3,6])); nitrous acid reacts *in situ* with the R-salt under formation of 1-nitroso-2-naphthol-3,6-disulfonic acid which appears in alkaline medium as a yellow-green spot. Instead of the R-salt solution a solution of 2-naphtholate can be used for spraying with the same effect (without the necessity of developing in ammonia gas, since the yellow-green spot of 1-nitroso-2-naphthol appears immediately after spraying).

The finding that synthetic compound *IV* reacts under the effect of ammonia (or other base) with the R-salt present or with 2-naphthol under formation of the corresponding nitroso compound proves that in the first phase of the detection of sulfinic acid (under the effect of nitrous gases) N,N-diarylsulfonyl-hydroxylamine is formed.

The identification of the nitroso compound formed *via* the N,N-diarylsulfonylhydroxylamine was carried out on reaction of *IV* with 2-naphthol in acetone solution in the presence of ammonia; the green precipitate formed gives a characteristic reaction of aromatic nitroso compounds[7,8] with sodium pentacyanoammoferroate ($Na_3[Fe(CN)_5NH_3]$).

Finally a chromatographic proof of the formation of 1-nitroso-2-naphthol-3,6-disulfonic acid was carried out when authentic preparations and R-salt were used, and of 1-nitroso-2-naphthol when 2-naphtholate was used for detection.

The proposed detection method was checked by chromatography of these sulfinic acids: benzenesulfinic, *p*-toluenesulfinic, *p*-acetaminobenzenesulfinic and *m*-nitrobenzenesulfinic acid. Chromatography was carried out in five solvent systems: S_1 (1-propanol–ammonia 2 : 1), S_2 (1-propanol–water 2 : 1), S_3 (1-propanol–1-butanol–ammonia 1 : 1 : 1), S_4 (1-propanol–1-butanol–water 1 : 1 : 1), and S_5 (1-propanol–water 3 : 1). The R_F values decrease in the order mentioned (Table I).

TABLE I

R_F Values of Sulfinic Acids ($R—SO_2H$) in the Solvent Systems S_1—S_5 (24°C)

R—	S_1	S_2	S_3	S_4^a	S_5
C_6H_5–	0·77	0·72	0·65	0·60	0·50
p-$H_3C.C_6H_4$–	0·81	0·78	0·69	0·67	0·55
p-$H_3CCONH.C_6H_4$–	0·71	0·66	0·50	0·48	0·38
m-$O_2N.C_6H_4$–	0·79	0·75	0·66	0·60	0·51

[a] The system was also used by Gringras and coworkers[1].

The relative positions of the spots of the sulfinic acids tested are approximately equal in all the five solvent mixtures. In all instances the spots are clearly yellow-green and sharply contoured; after several days the spots disappear and therefore their position should be indicated in pencil on the chromatogram after detection.

The proposed detection can be used for the identification of sulfinic acids in addition to sulfonic acids; if the spots do not interfere the detection may be used for their identification in the presence of diazotizable amines and their derivatives.

Since we observed the possibility of this detection for the first time with *m*-nitrobenzenesulfinic acid, compound *IV* was prepared first for the study of the chemistry of the detection. In literature two methods of preparation of N,N-diarylsulfonyl-hydroxylamine are described, *i.e.* under the effect of nitrous acid on sulfinic acids in aqueous medium[3-5], or under the effect of alkyl nitrite on sulfinic acids in ether solution[9]. In our case of the preparation of *IV* it seemed more logical to operate in aqueous medium. We then synthetized compound *III* in an analogous manner.

EXPERIMENTAL

Material: The sulfinic acids used were prepared by known methods of reduction of corresponding sulfonyl chlorides: benzenesulfinic acid[10] and *p*-acetaminobenzenesulfinic acid[11] with sodium sulfite, *p*-toluenesulfinic acid[12] with zinc, and *m*-nitrobenzenesulfinic acid[13] with stannous chloride and HCl in absolute ethanol.

Chromatography: Sulfinic acids were applied on Whatman No 1 chromatographic paper in the form of solutions in water–pyridine mixture or in aqueous solutions of sodium salts were used. The development of the chromatograms was carried out in the descending manner at 24°C. After development (about 20 cm running distance) and drying the chromatogram was first immersed for about 1 minute in nitrous gases (which were liberated by acidification of a 2·5M-$NaNO_2$ solution with hydrochloric acid), then sprayed with an aqueous solution of R-salt and hung over conc. ammonia in a tank (this is in principle the same procedure as used in the detection of aromatic primary amines[14,15]). If the spraying with a solution of 2-naptholate is used the exposure to ammonia vapours is not necessary.

Proof of the formation of N,N-*diarylsulfonyl-hydroxylamine in the first phase of detection*: Drops of a solution of *IV* in acetone were left to dry and then drops of aqueous solution of the R-salt were applied onto them on one hand or drops of an acetone solution of 2-naphthol on the other; when exposed to ammonia gas or on application of a solution of sodium carbonate characteristic yellow-green spots appeared immediately.

Identification of the nitroso compound formed via N,N-*diarylsulfonylhydroxylamine*: About 0·1 g of *IV* was dissolved in 2 ml of acetone, a solution of the same amount of 2-naphthol in 2 ml of acetone was added, the mixture cooled below 10°C and alkalized by addition of an excess of aqueous ammonia. After neutralization the precipitate was filtered off and washed with water. After warming with 1% solution of sodium pentacyanoammoferroate the precipitate gives an intensive green coloration the same as with 1-nitroso-2-naphthol.

Chromatographic proof of the formation of 1-*nitroso*-2-*naphthol*-3,6-*disulfonic acid or of* 1-*nitroso*-2-*naphthol during the detection*: A solution of *IV* in acetone was applied on Whatman No 1paper and a drop of a solution of 2-naphthol was put on it in the first case and of a solution of the R-salt in the second. Parallelly solutions of 1-nitroso-2-naphthol and 1-nitroso-2-naphthol-3,6-disulfonic acid were also applied onto the start. After drying the chromatogram was developed in the descending manner in S_1. As soon as the ammoniacal system reached the start compound *IV* decomposed and the nitrous acid set free nitrosated the 2-naphthol or the R-salt present. After development (17 cm) the 1-nitroso-2-naphthol formed had R_F 0·81 and the 1-nitroso-2-naphthol-3,6-disulfonic acid formed R_F 0·12; both these values were in complete agreement with the R_F values of the simultaneously chromatographed authentic preparations (all spots were yellow-green).

If a strip was cut off the developed chromatogram on which 1-nitroso-2-naphthol-3,6-disulfonic acid formed on the start by decomposition of *IV* was chromatographed, and detected using the method proposed for sulfinic acids, the cleaved *m*-nitrobenzenesulfinic acid could also be detected (yellow-green spot of R_F 0·79).

Preparation of N,N-*di*(m-*nitrobenzenesulfonyl*)*hydroxylamine* (IV): *m*-Nitrobenzenesulfinic acid (3·74 g; 0·02 mol) in the form of its sodium salt (5·88 g, *i.e.* with 63·7% of the free acid) was dissolved in 100 ml of water, 10 ml of M-$NaNO_2$ (0·01 mol) was added and the solution cooled externally to 0°C. Concentrated hydrochloric acid (3 ml) was then added dropwise over about 15 min under constant cooling and stirring. The stirring was continued for another 30 min at 0°C and left to stand overnight. The crystalline product was filtered off and washed with water until neutral and until the reaction on chlorides in the filtrate was negative. After drying over P_2O_5 3·8 g of a product were obtained (94·3%) in the form of white small prisms (from methanol in the cold), m.p. 108°C (decomp.), uncorr.

The substance is practically insoluble in water, very well soluble in methanol, ethanol, acetone; poorly soluble in hot benzene. For $C_{12}H_9N_3O_9S_2$ (403·4) calculated: 35·73% C, 2·25% H, 15·90% S; found: 35·94% C, 2·40% H, 15·69% S.

Preparation of N,N-*di*(p-*acetaminobenzenesulfonyl*)-*hydroxylamine* (III): *p*-Acetaminobenzenesulfinic acid (15·92 g; 0·08 mol) in the form of its sodium salt (24·6 g, with 64·7% of free acid) was dissolved in 60 ml of water, 16 ml of 2·5M-$NaNO_2$ (0·04 mol) was added, the mixture was cooled to 5°C and conc. HCl (11 ml) was added dropwise. The precipitated finely crystalline product was filtered off and washed with water until neutral and there was a negative reaction for chlorides in the filtrate. After drying over P_2O_5 14·5 g of a product were obtained (84·7%) in the form of white prisms (from dimethylformamide), m.p. 193—195°C (decomp.), uncorr. During recrystallization from dimethylformamide the substance evidently decomposed. The uncrystallized product (14·5 g) was purified by a triple decantation with water and washing with ethanol and finally with ether. It had m.p. 204—206°C (decomp.), uncorr., which is higher than that of the recrystallized compound; the mixture melting point of the recrystallized product with the product purified in the above manner was undepressed. The elemental analysis was therefore carried out with the uncrystallized compound.

The substance is poorly soluble in hot water, acetone and methanol, insoluble in ether, chloroform and benzene; it is very well soluble in dimethylformamide. For $C_{16}H_{17}N_3O_7S_2$ (427·5) calculated: 44·95% C, 4·02% H, 9·83% N, 15·00% S; found: 45·80% C, 4·13% H, 9·53% N, 15·10% S.

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