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THE FIRST ISOLATION AND CHARACTERIZATION OF FREE PHENYLAMIDOSULFURIC ACID AND ITS RING-SUBSTITUTED DERIVATIVES. POSTULATED INTERMEDIATES IN THE SULFONATION OF AROMATIC AMINES

Fujio KANETANI
Department of Applied Chemistry, Faculty of Engineering,
Hiroshima University, 3-8-2, Senda-machi, Hiroshima, 730

Thirteen free arylamidosulfuric acids were prepared and charactrized for the first time. These acids could readily been obtained in a pure state simply by adding concentrated hydrochloric acid to a cold aqueous solution of the corresponding ammonium salts. These compounds are non-hygroscopic, crystalline solids and quite stable at room temperature under anhydrous conditions. The spectral data clearly showed that all the arylamidosulfuric acids exist as zwitterions, $ArNH_2^+-SO_3^-$, in the solid state.

Phenylamidosulfuric acid has been postulated as an intermediate in the sulfonation of aniline with sulfuric acid or by the so-called baking process.[1-3] However, this acid has never been isolated as such from these reactions[1,3c,4-6] nor been prepared.[4-7]

Amidosulfuric acid and its N-alkyl and N-cycloalkyl derivatives are fairly resistant to both hydrolytic and thermal cleavage of the N-S bond and can easily be obtained in the pure state, whereas arylamidosuluric acids are much more susceptible to hydrolysis and therefore always isolated as salts.[4,7,8]

Although a number of claims for the isolation of free arylamidosulfuric acids have hitherto been made in the literature,[9-17] careful inspection of these claims reveals that most of them have been disproved, or seriously disputed by later workers,[7,15,18] or they are not in accord with accumulated facts which indicate that the acids claimed should not be isolable under the conditions reported.[16-17]

In this communication, we report the first definite isolation and characterization of free phenylamidosulfuric acid (1) and its ring-substituted derivatives.

Procedure[19]

To a stirred ice-cold solution of ammonium phenylamidosulfate dissolved in the minimum volume of water was added an equal volume of cold concentrated hydrochloric acid, whereupon the crystals separated. These were collected by suction filtration, washed with cold 6N hydrochloric acid, spread out and pressed well on a porous plate, and dried in a vacuum desiccator. The product was again dissolved in the minimum amount of ice-cold water. To the clear solution,[20] cold concentrated hydrochloric acid was added with stirring and the crystals separated were filtered, washed, and dried in a vacuum desiccator. Other arylamidosulfuric acids were prepared similarly.

The free acid (1) thus obtained was a non-hygroscopic, colorless, crystalline solid which had no definite melting point owing to the facile thermal rearrangement into ring-sulfonated products. (1) was readily soluble in water, alcohol, and acetone, and practically insoluble in ether, chloroform, benzene, and ethyl

Table Arylamidosulfuric Acids, $ArNH_2^+-SO_3^-$

Ar	Formula		Elemental Analysis			IR (KBr) cm^{-1}			
			C	H	N	$\delta(NH_3)$	$\nu_{as}(SO_3)$	$\nu_s(SO_3)$	other bands.
C_6H_5	$C_6H_7NO_3S$	calcd	41.61	4.07	8.09	1546	1359 1303	1050	1494 1475
	(173.19)	found	41.68	4.14	8.14		1256		769 689
3-MeC_6H_4	$C_7H_9NO_3S$	calcd	44.91	4.85	7.48	1580	1365 1328	1061	1500 783
	(187.22)	found	44.55	4.80	7.54		1298 1278		741 690
4-MeC_6H_4	$C_7H_9NO_3S$	calcd	44.91	4.85	7.48	1541	1361 1312	1054	1512 819
	(187.22)	found	44.90	4.80	7.26		1260		750
2,6-$Me_2C_6H_3$	$C_8H_{11}NO_3S$	calcd	47.75	5.51	6.96	1565	1337 1312	1061	1475 769
	(200.24)	found	47.81	5.70	6.93		1272		
3,5-$Me_2C_6H_3$	$C_8H_{11}NO_3S$	calcd	47.75	5.51	6.96		1353 1330	1055	1527 856
	(200.24)	found	47.92	5.42	6.89		1309 1265		696 656
2,4,5-$Me_3C_6H_2$	$C_9H_{13}NO_3S$	calcd	50.22	6.09	6.51	1539	1350 1321	1048	1510 1221
	(213.25)	found	50.31	6.12	6.48		1286		893
2,4,6-$Me_3C_6H_2$	$C_9H_{13}NO_3S$	calcd	50.22	6.09	6.51	1560	1339 1273	1062	1480 858
	(213.25)	found	50.42	6.07	6.53				775 724
2-$MeOC_6H_4$	$C_7H_9NO_4S$	calcd	41.37	4.46	6.89		1333 1287	1050	1503 1469
	(203.22)	found	41.30	4.40	6.67		1265		890 775
4-HOC_6H_4	$C_6H_7NO_4S$	calcd	38.09	3.73	7.40	1550	1358 1311	1065	1605 1518
	(189.19)	found	38.17	3.60	7.35				1474 835
2-$HOOCC_6H_4$	$C_7H_7NO_5S\cdot H_2O$	calcd	35.74	3.86	5.95	1554	1315	1102	1688 1466
	(235.22)	found	36.11	4.16	5.94				832 752
3-$MeCOC_6H_4$	$C_8H_9NO_4S$	calcd	44.64	4.22	6.51		1306 1280	1051	1648 1380
	(215.23)	found	44.00	4.17	6.39				810 764
α-Naphthyl	$C_{10}H_9NO_3S\cdot 1/_2H_2O$	calcd	51.71	4.34	6.03	1573	1343 1309	1056	802 770
	(232.26)	found	51.40	4.26	5.92		1263		
β-Naphthyl	$C_{10}H_9NO_3S$	calcd	53.80	4.06	6.27	1581	1363 1324	1061	819 747
	(223.25)	found	53.50	3.85	5.99		1306 1282		

acetate. A freshly prepared solution of (1) gave only a slight turbidity with barium ion.

Contrary to the statement of Hurd and Kharasch,[7,21] IR spectral data clearly demonstrate that arylamidosulfuric acids, as well as amidosulfuric acid and its N-alkyl derivatives,[22,23] exist as zwitterions, $\mathrm{ArNH_2^+\text{-}SO_3^-}$, in the solid state; that is, all the arylamidosulfuric acids showed strong absorption bands at 1260-1315 and 1330-1360 $\mathrm{cm^{-1}}$ due to $\mathrm{SO_3^-}$ degenerate stretching vibrations of the $\geqslant\mathrm{N^+\text{-}SO_3^-}$ grouping.[23]

Furthermore, it should be noted that, in contrast with the "baking" of anilinium hydrogen sulfate, thermal rearrangement of (1) in dioxane gave considerable amounts of o-aminobenzenesulfonic and 4-amino-1,3-benzenedisulfonic acids in addition to sulfanilic acid (TLC analysis).[24]

References and Notes

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19) This prodedure should be carried out as quickly as possible, because the hydrolysis is accelerated markedly by the presence of hydrochloric acid.
20) Silk-like glistening crystals separated when the solution was kept in the ice-bath for about half an hour. This substance, which is much less soluble than free phenylamidosulfuric acid (1), proved to be phenylammonium phenylamidosulfate (2). This is probably produced according to the following scheme:

$$\underset{(\underline{1})}{C_6H_5NH_2{}^+SO_3{}^-} + H_2O \longrightarrow C_6H_5NH_3{}^+HSO_4{}^-$$

$$\underset{(\underline{1})}{C_6H_5NH_2{}^+SO_3{}^-} + C_6H_5NH_3{}^+HSO_4{}^- \longrightarrow \underset{(\underline{2})}{C_6H_5NHSO_3{}^-C_6H_5NH_3{}^+} + H_2SO_4$$

21) C. D. Hurd and N. Kharasch, J. Am. Chem. Soc., 68, 653 (1946).

22) It has been well established that amidosulfuric acid exists in a solid state as a zwitterion, $NH_3{}^+\text{-}SO_3{}^-$,[a] whereas its salts exist as the amidosulfate ion, $NH_2SO_3{}^-$ [b] [a) R. L. Sass, Acta Crystallogr., 13, 320 (1960) and references cited therein; b) B. E. Cain and F. K. Kanda, Z. Krystallogr., Krystallgeom., Krystallphys., Krystallchem., 135, 253 (1972); V. K. Wadhawan and V. M. Padmanabhan, Acta Crysallogr., Sect. B, 28, 1903 (1972).].

23) IR spectra of amidosulfuric acid and a number of its N-alkyl and N-cycloalkyl compounds exhibit strong absorption bands generally at 1280-1320 and 1055-1080 cm^{-1} due to $SO_3{}^-$ degenerate and symmetric stretching vibrations, respectively; on the other hand, their salts absorbs at 1185-1220 and 1040-1060 cm^{-1} [H. Siebert, Z. Anorg. Allg. Chem., 292, 167 (1957); E. Steger, ibid., 325, 89 (1963) and references cited therein; unpublished data in our laboratory].

24) This finding suggests that (1) may not be an intermediate in the baking process. The intermediacy of dianilinium disulfate as a more plausible alternative will be discussed later.

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