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Abstract

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The Action of Acid Chlorides of Inorganic Acids on Arylsulfonic Acids

A General Method for Preparing Anhydrides by the Reaction of Arylsulfonic Acids with P_2O_5

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It is well known that the most common methods for converting arylsulfonic acids into sulfonyl chlorides are based on treating the sodium or potassium salts of sulfonic acids with phosphorus pentachloride, more rarely with phosphorus oxychloride; chlorosulfonic acid is usually applied directly to unsulfonated substances. Among other acid chlorides, for example PCl_3, $SOCl_2$, $COCl_2$ (some of which, incidentally, are very commonly used for preparing acid chlorides of carboxylic acids), thionyl chloride attracts attention by the results of its action. According to the data of Hans Meyer ([1]), when thionyl chloride is boiled with sulfonic acids or their salts, anhydrides of sulfonic acids are often obtained along with sulfonyl chlorides; in the author' s conclusion, sulfonyl chlorides and anhydrides are formed essentially independently of one another.

Judging from the literature, in the interaction of sulfonic acids with phosphorus pentachloride the formation of anhydrides is also possible as an exception. This occurs, for example, in the case of *o*-disulfonic acid of *p*-xylene ([2]) and the sulfonic acid of *p*-diiodobenzene ([3]). On the basis of our observations, however, it appears that the formation of anhydrides under the action of phosphorus pentachloride on sulfonic acids or their salts is a fairly widespread phenomenon: Table 1 gives the results of this reaction for a series of compounds.

The sulfonic acid (0.01 mole), usually containing 1 mole of water of crystallization, or the corresponding amount of its anhydrous sodium salt, is moistened with phosphorus oxychloride (1 ml), and PCl_5 in powder form (4.0 g) is added at once. With sulfonic acids, in a number of cases an energetic reaction begins almost immediately; the mass heats to 35–40° and liquefies. Sodium salts react more slowly (see experiments 4, 6, 7). After the time indicated in the table has elapsed, the semiliquid mass is poured into a flask with ice, shaken vigorously, and the solidified comminuted product is filtered off, washed with water, and dried on a funnel by drawing air through the precipitate at room temperature. The anhydride and sulfonyl chloride are separated with the aid of glacial acetic acid or ether, in which the solubility of the anhydrides is insignificant. We have

established that the anhydrides of sulfonic acids are formed before the reaction mixtures are treated with water. If, for example, in experiment 3 (with the sulfonic acid) the mass is diluted with a small amount of $POCl_3$ (2 ml), filtered off, and washed with absolute ether, the amount of anhydride obtained is about 40% of theory. Furthermore, the anhydrides of sulfonic acids are almost unchanged under brief action of PCl_5 in a mixture with $POCl_3$ (10 min, 30°). Finally, under these conditions the possibility is excluded of formation of anhydrides of sulfonic acids by the action of sulfonyl chlorides on sulfonic acids or their salts (the route for preparing anhydrides of carboxylic acids). Therefore it may be assumed that the mechanism of formation of sulfochlorides and sulfonic acid anhydrides, starting from sulfonic acids or their salts, is represented by the following schemes:

$$RSO_3H + PCl_5 \rightarrow RSO_2 \cdot O \cdot PCl_4 + HCl \rightarrow RSO_2Cl + POCl_3 + 2HCl \quad (1)$$

$$RSO_2 \cdot O \cdot PCl_4 + RSO_3H \rightarrow \begin{matrix} RSO_2 \cdot O \cdot \\ RSO_2 \cdot O \cdot \end{matrix} PCl_3 + HCl \rightarrow (RSO_2)_2O + POCl_3 + HCl \quad (2)$$

The process of formation of sulfonic acid anhydrides proceeds analogously in the reaction with thionyl chloride:

$$RSO_2O \cdot SOCl + RSO_3H \rightarrow \begin{matrix} RSO_2 \cdot O \cdot \\ RSO_2 \cdot O \cdot \end{matrix} SO + HCl \rightarrow (RSO_2)_2O + SO_2 + HCl \quad (3)$$

Table 1

Experiment no.	Radical of sulfonic acid	Experiments with sulfonic acid: duration of experiment, min	Experiments with sulfonic acid: anhydride, % theoretical	Experiments with sulfonic acid: sulfochloride, % theoretical	Experiments with Na salt of sulfonic acid: duration of experiment, min	Experiments with Na salt of sulfonic acid: anhydride, % theoretical	Experiments with Na salt of sulfonic acid: sulfochloride, % theoretical
1	4-ClC_6H_4–	5	5.4	83.0	5	none	93.0
2	2,4-$Cl_2C_6H_3$–	–	–	–	15	7.3	90.0
3	2,5-$Cl_2C_6H_3$–	5	59.3	33.0	10	8.1	85.0

Experiment no.	Radical of sulfonic acid	Experiments with sulfonic acid: duration of experiment, min	Experiments with sulfonic acid: anhydride, % theoretical	Experiments with sulfonic acid: sulfochloride, % theoretical	Experiments with Na salt of sulfonic acid: duration of experiment, min	Experiments with Na salt of sulfonic acid: anhydride, % theoretical	Experiments with Na salt of sulfonic acid: sulfochloride, % theoretical
4	$2,3,5,6\text{-}Cl_4C_6H$–	5	40.7	55.4	90	none	98.5
5	$2,4\text{-}Br_2C_6H_3$–	5	38.2	49.3	15	5.8	91.8
6	$2,5\text{-}Br_2C_6H_3$–	5	34.7	62.2	20	3.3	68.5
7	$3\text{-}(NO_2)C_6H_4$–	5	26.3	62.7	10	none	53.9
8	$4\text{-}CH_3C_6H_4$–	5	16.6	73.9	5	none	97.9
9	$2,4\text{-}(CH_3)_2C_6H_3$–	5	38.1	60.1	5	15.2	84.6
10	$2,5\text{-}(CH_3)_2C_6H_3$–	5	28.0	68.2	5	1.0	84.0
11	$2,4,6\text{-}(CH_3)_3C_6H_2$–	6	61.6	29.4	6	34.0	60.4

These schemes express the fact that the process of "reanhydridization" –in our cases, the transition from acid chlorides of inorganic acids to arylsulfonic acid chlorides or anhydrides–is accomplished through the corresponding mixed anhydrides (analogously to the formation of acid chlorides and anhydrides of carboxylic acids).

Phosphorus oxychloride reacts with free sulfonic acids and their sodium salts considerably more slowly than PCl_5; moreover, with the salts, exclusively sulfochlorides are formed, whereas with sulfonic acids anhydrides are also often formed (Table 2). In all experiments the sulfonic acid (0.01 mole), containing 1 or 2 moles of water of crystallization, was heated for 1 hour with $POCl_3$ (4.0 ml) at 104–106°, after which the mixture was cooled and decomposed with water and ice, as indicated above.

The sodium salts of sulfonic acids react only very slowly with boiling phosphorus trichloride. Exceptions are the salts of mesitylene- and 2,4,6-triethylbenzenesulfonic acids when they contain about 1 mole of water of crystallization (calculated). In these two cases, just as with the free sulfonic acids, sulfonic acid anhydrides are formed predominantly (Table 2). In all experiments, 4.0 ml of PCl_3 was taken per 0.01 mole of sulfonic acid.

Is it possible to obtain sulfonic acid anhydrides by the interaction of sulfonic acids with chlorosulfonic acid?

Recently ([4]) we showed that here, just as with the acid chlorides of other inorganic acids, mixed anhydrides $RSO_2 \cdot O \cdot SO_3H$ are formed in the first stage,

as a result of which, it would seem, the prerequisites are created for further interaction according to the scheme:

$$RSO_2 \cdot O \cdot SO_3H + RSO_3H \rightleftarrows (RSO_2)_2O + H_2SO_4. \quad (4)$$

In reality, however, the anhydrides react further very readily with chlorosulfonic acid; therefore, except in the special cases considered below, their accumulation is impossible. One can conceive of two courses for this process in the initial stage:

$$O + ClSO_3H \rightleftarrows \begin{matrix} RSO_2 \\ RSO_2Cl \end{matrix} + \begin{matrix} RSO_2 \\ RSO_2 \cdot O \cdot SO_3H \end{matrix} \quad (6)$$

and

$$O + ClSO_3H \rightleftarrows \begin{matrix} RSO_2 \\ RSO_3H \end{matrix} + \begin{matrix} RSO_2 \\ RSO_2 \cdot O \cdot SO_2Cl \end{matrix} \quad (7)$$

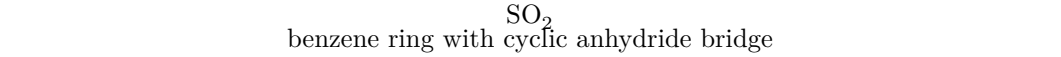
Table 2

Experiment No.	Sulfonic-acid radical	Experiments with $POCl_3$: anhydride, % theory	Experiments with $POCl_3$: sulfochloride, % theory	Experiments with PCl_3: duration, hours	Experiments with PCl_3: anhydride, % theory	Experiments with PCl_3: sulfochloride, % theory
1	C_6H_5-	20.0	68.0	2	28.2	2.3
2	$4-ClC_6H_4-$	49.2	41.8	2	32.7	3.0
3	$2,5-Cl_2C_6H_3-$	66.5	18.8	2	10.5	traces
4	$3-(NO_2)C_6H_4-$	51.5	13.5	2	9.0	»
5	$2,4-(CH_3)_2C_6H_3-$	—	98.0	1	40.0	»
6	$2,4,6-(CH_3)_3C_6H_2-$	—	98.5	1	63.0	7.4
7	$C_{10}H_7-1-$	—	98.0	1	42.5	10.2
8	$C_{10}H_7-2-$	—	86.5	1	38.5	22.1

In the first case, one half of the amount of anhydride taken should be converted into the sulfochloride immediately after dissolution of the anhydride in a large excess of $ClSO_3H$. According to our observations, the sulfonic acids

corresponding to the anhydrides react with $ClSO_3H$ more slowly than do the anhydrides; therefore, if scheme (7) is correct, in the reaction mixture, at the first moment after dissolution of the anhydride, there might not be an amount of sulfochloride corresponding to one half of the anhydride taken. This question was resolved experimentally with the aid of the anhydrides of *o*-dichlorobenzene- and *m*-nitrobenzenesulfonic acids. We give the experiment with the anhydride of *m*-nitrobenzenesulfonic acid: the finely powdered substance (0.00125 mole) in a test tube is treated, with stirring, with chlorosulfonic acid (3 ml) cooled to 0°, and after 20-30 sec the mixture is poured onto ice, giving an almost clear solution with traces of *m*-nitrobenzenesulfochloride. Thus, only scheme (7) can be valid.

The literature describes the formation of the anhydride of benzene-*o*-disulfonic acid



benzene ring with cyclic anhydride bridge

by the reaction of chlorosulfonic acid with the dipotassium salt of *o*-disulfonic acid at 120° (5). It should be assumed that the possibility of obtaining this internal anhydride is due to its resistance to the action of hot $ClSO_3H$, together with the extreme instability of the intermediately formed mixed anhydride

$$SO_2 \cdot O \cdot SO_3H$$

$$C_6H_5\text{-}SO_3H$$

which, as it arises, immediately cyclizes.

In conclusion we shall describe a general method for obtaining anhydrides of sulfonic acids by the action of phosphorus anhydride on sulfonic acids in chloroform, remembering, in this connection, that in a hydrocarbon medium the corresponding sulfones may form ([6]).

Methods based on the interaction of sulfonic acids with acid chlorides of inorganic acids or on sulfonation with oleum (for the literature see ([7])) by no means always lead to anhydrides, which, moreover, are usually contaminated with impurities of sulfochlorides, sulfonic acids, and sulfones, making their isolation in the pure state difficult. Phosphorus pentoxide has been tested, without particular success, for obtaining the anhydride of *o*-sulfobenzoic acid ([8]); cases have recently been described of the use of P_2O_5 for obtaining anhydrides of methane- and ethanesulfonic acids, as well as benzene- and *p*-toluenesulfonic acids ([10]); the yields of the last two anhydrides are low—about 50% of theory, possibly owing to overheating of the reaction mixture.

Our procedure is as follows: the sulfonic acid (0.02 mol), containing 1 or 2 mol of water of crystallization, is suspended in abs. chloroform (15–25 ml), and

powdered P_2O_5 is gradually added in large excess (6-10 g), from time to time rubbing the precipitate. To complete the reaction, prolonged boiling is required (up to 30 min). The sign of the end of the reaction is complete decolorization of the solution. The subsequent procedure is twofold: readily soluble

Table 3

Experiment no.	Aromatic radical of the sulfonic acid	Anhydride: yield, % of theory	Anhydride: m.p., °C	Anhydride: crystal form (from chloroform or chlorobenzene)
1	C_6H_5-	80	90-92	Four-sided prisms
2	$4-ClC_6H_4-$	85.5	ca. 150	Four-sided prisms or multi-faceted crystals
3	$3,4-Cl_2C_6H_3-$	90	118-119	Quadrangular plates or prisms
4	$2,4-Cl_2C_6H_3-$	86	190-195	Four-sided prisms
5	$4-BrC_6H_4-$	88	170-180	Four-sided prisms
6	$3,4-Br_2C_6H_3-$	84	163	Short prisms
7	$2,4-Br_2C_6H_3-$	89	225-230	Four-sided prisms
8	$3-(NO_2)C_6H_4-$	80	ca. 160	Plates
9	$4-CH_3C_6H_4-$	90	125-130	Parallelepipeds
10	$3,4-(CH_3)_2C_6H_3-$	86	137-140	Four-sided prisms
11	$2,4-(CH_3)_2C_6H_3-$	93	153-156	Multifaceted crystals
12	$2,5-(CH_3)_2C_6H_3-$	90	126-128	Dense plates or prisms
13	$2,4,6-(CH_3)_3C_6H_2-$	88	ca. 225	Four-sided prisms
14	$C_{10}H_7-1-$	84.5	ca. 210	Four-sided prisms

Experiment no.	Aromatic radical of the sulfonic acid	Anhydride: yield, % of theory	Anhydride: m.p., °C	Anhydride: crystal form (from chloroform or chlorobenzene)
15	$C_{10}H_7$—2—	82	185-190	Quadrangular plates or prisms
16	$C_{14}H_7O_2$—1—	56	245-250	Indeterminate
17	$C_{14}H_7O_2$—2—	40	ca. 250	Warty

anhydrides are taken up in chloroform, the solvent is completely evaporated in vacuo, and the crystalline anhydride residue is washed with glacial acetic acid and ether. In the remaining cases, the reaction mass is treated with water and ice; the anhydride precipitate is filtered off and washed as above. The anhydrides of α- and β-anthraquinonesulfonic acids have a faint yellowish color; the others are snow-white.

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