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Abstract

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ON QUESTIONS OF SULFONATION IN THE AROMATIC SERIES

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In the processes of formation of sulfochlorides, sulfones, and anhydrides of sulfonic acids obtained in the sulfonation of compounds of the aromatic series, an important role is played, in our opinion, by intermediate substances—mixed anhydrides $ArSO_2 \cdot O \cdot SO_2OH$—products of the addition of SO_3 to molecules of arylsulfonic acids, which are sometimes represented by the formula ArS_2O_6H and, apparently, are regarded as substances of low reactivity (^{1}). Starting from this assumption, we wish to examine, using several examples, sulfonation with chlorosulfonic acid and with oleum.

It is well known that chlorosulfonic acid is widely used for obtaining sulfochlorides, the yields of which, under optimal operating conditions, often exceed 80-85% of theoretical. We are now interested, however, in quite different results, which occur with a sharp lowering of the temperature and a certain increase in the excess of $ClSO_3H$ in order to reduce the duration of sulfonation.

The substance to be sulfonated is added to $ClSO_3H$ uniformly over 1 hour, after which stirring is continued for the time indicated in Table 1; in expts. 5, 6, 8, and 9—for half an hour at 5° and 1 hour at 10°, in expt. 7—for 2.5 hours at 25°. In the last experiment, 38.8% of *p*-dichlorobenzene remains. The mixture is then poured onto ice,

Table 1

No. of expt.	Aromatic radicals of the sulfonic acids	Reaction conditions	Reaction conditions	Reaction conditions	Yield, %	Yield, %	Yield, %
		temperature, °C	duration, hours	amount of $ClSO_3H$, mol	sulfochloride	sulfone	sulfonic acid

No. of expt.	Aromatic radicals of the sulfonic acids	Reaction conditions	Reaction conditions	Reaction conditions	Yield, %	Yield, %	Yield, %
1	C_6H_5—	−8, −5	1.5	2.7	19.2	29.9	46.3
2	4-ClC_6H_4—	−8, −5	1.3	3.9	17.5	29.4	50.3
3	4-BrC_6H_4—	−8, −6	1.3	3.9	16.0	38.1	42.5
4	4-IC_6H_4—	−10, −8	1.2	3.9	16.7	41.5	38.5
5	3, 4-$Cl_2C_6H_3$—	0 (5–10)	2.5	4.7	24.5	23.9	44.8
6	2, 4-$Cl_2C_6H_3$—	0 (5–10)	2.5	4.7	23.3	6.1	63.8
7	2, 5-$Cl_2C_6H_3$—	20 (25)	3.5	4.7	45.4	—	48.5
8	3, 4-$Br_2C_6H_3$—	0 (5–10)	2.5	4.7	26.6	25.0	41.5
9	2, 4-$Br_2C_6H_3$—	0 (5–10)	2.5	4.7	22	5.9	62.0

the solidified portion is separated, washed with ether and water, yielding the principal portion of the sulfone. The ether solution is dried, the ether is evaporated, and from the remaining mass the sulfochloride is isolated by distillation in vacuo. The residue is boiled with dilute caustic soda solution, determining the additional amounts of sulfochloride and sulfone. In experiments 1-5 and 7, the aqueous-acid solution is treated with gypsum; the calcium salts are converted into sodium salts, and part of the sodium salt is converted into the sulfochloride with the aid of PCl_5. In the remaining experiments, the aqueous-acid portion is saturated with sodium chloride, whereby almost all the sulfonic acid is isolated in the form of the sodium salt.

The experimental results are summarized in Table 1.

As the principal products, as is evident from Table 1, sulfonic acids and sulfones are obtained; as regards the sulfochlorides, it is not difficult to con-

···that they appear as the result of a secondary reaction of sulfonic acids with $ClSO_3H$: the figures in Table 2 give an idea of how significant the amounts of sulfonyl chlorides are that formed after a 60-minute residence of individual sulfonic acids in a mixture of $ClSO_3H$ and H_2SO_4. The ratios of reagents in the first five experiments correspond to the ratios in the corresponding experiments of Table 1, established at the very end of sulfonation*.

Table 2

Experiment Nos.	Aromatic radicals of sulfonic acids	Temperature, °C	Sulfonic acid, mol	$ClSO_3H$, mol	H_2SO_4, mol	Sulfonyl chloride, mol. % relative to the starting sulfonic acid
1	C_6H_5—	−8, −6	1.0	1.7	1.0	43.6
2	4-ClC_6H_4—	−8, −6	1.0	2.9	1.0	55.0 (18.7)
3	4-BrC_6H_4—	−8, −6	1.0	2.9	1.0	47.1 (20.8)
5	3, 4-$Cl_2C_6H_3$—	10	1.0	3.7	1.0	55.0 (17.0)
6	2, 4-$Cl_2C_6H_3$—	10	1.0	3.7	1.0	48.0 (24.3)
7	2, 5-$C_2C_6H_3$—	15—17 (2 h)	1.0	7.3	1.0	55.6 (3.8)
[[unclear: experiment number]]	3-(NO_2)C_6H_4—	15—23 (5 h)	1.0	6.1	1.0	45.0 (6.9)

We thus see that, upon sulfonation with chlorosulfonic acid, sulfonic acids are first formed, which subsequently, under the action of excess $ClSO_3H$, are converted into sulfonyl chlorides. This conclusion is in agreement with the considerations of some other investigators ([2]).

Noteworthy is the formation of abundant amounts of sulfones at low temperatures, in particular under the conditions of our experiments. If one assumes that sulfones are obtained as a result of sulfonation by sulfonic acids of the initial unsulfonated compounds ([3]), then the role of $ClSO_3H$ in this process must be reduced to binding the reaction water in order to keep the sulfonic acids in the anhydrous state. In doing so, however, we are forced to attribute to sulfonic acids an incredible capacity: in terms of sulfonating action, to compete successfully with $ClSO_3H$. No less strange is the fact (as follows from the data of Table 3) that the main portion of the sulfones arises in the initial period of sulfonation, when the amounts of sulfonic acids in the reaction mixtures are still relatively small.

Table 3

Experiment Nos.	Aromatic radicals of sulfonic acids	$ClSO_3H$, mol	H_2SO_4, mol	Substance being sulfonated, %	Sulfonyl chloride, %	Sulfone, %
1	C_6H_5—	1.7	1.0	–	0.8	10.5
3	4-ClC_6H_4—	2.9	1.0	–	1.6	7.2
3′	4-ClC_6H_4—	1.9	2.0	10	0.3	1.8
3″	4-ClC_6H_4—	1.0	2.9	30	0.14	0.3
4	4-BrC_6H_4—	2.5	1.5	traces	1.0	5.3
6	3, 4-$Cl_2C_6H_3$—	2.7	2.0	38	1.0	0.7
9	3, 4-$Br_2C_6H_3$—	3.7	1.0	20.7	3.7	3.5

Table 3 gives the results of sulfonation of certain substances with a mixture of $ClSO_3H$ and H_2SO_4; the conditions of the corresponding experiments in Tables 1 and 3 differ only in that, in the latter, part of the $ClSO_3H$ is replaced by an equimolar amount of 100% acid. First of all, it is evident that with such replacement a substantial portion of the starting substances remains unsulfonated (see experiments 3″, 6, and 9 in Table 3), which indicates the weaker sulfonating action of 100% H_2SO_4 in comparison with $ClSO_3H$. Further, replacement of part of the $ClSO_3H$ by 100% sulfuric acid leads to a sharp reduction in the yields of sulfones, although the $ClSO_3H$ remaining in the mixtures is more than sufficient to bind all the reaction water. And finally, sulfonyl chlorides are obtained, in essence, only in traces.

We see a close connection in the simultaneous decrease in the yields of sulfochlorides and sulfones, since we believe that both are produced by the mixed anhydrides formed as intermediates, arising according to scheme (1):

$$ArSO_3H + ClSO_3H \rightleftarrows ArSO_2 \cdot O \cdot SO_2OH + HCl. \tag{1}$$

The mixed anhydrides rapidly react further in two directions: with an excess of $ClSO_3H$ they give rise to sulfochlorides,

$$ArSO_2 \cdot O \cdot SO_2OH + ClSO_3H \rightleftarrows ArSO_2Cl + HOSO_2 \cdot O \cdot SO_2OH. \tag{2}$$

and, by sulfuring the starting substances, form sulfones,

$$ArSO_2 \cdot O \cdot SO_2OH + HAr \rightarrow ArSO_2Ar + H_2SO_4. \tag{3}$$

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* In all experiments we started from sulfonic acid anhydrides, dissolving them in calculated amounts of 92% H_2SO_4.

It is obvious that H_2SO_4 destroys mixed anhydrides by virtue of the existing equilibrium (4):

$$ArSO_2 \cdot O \cdot SO_2OH + H_2SO_4 \rightleftarrows ArSO_3H + HOSO_2 \cdot O \cdot SO_2OH, \qquad (4)$$

which also explains the sharp decrease in the amounts of sulfochlorides and sulfones with a considerable increase in the H_2SO_4 content in the reaction mixture.

It is very interesting that not only H_2SO_4, but also HCl, hinders the formation of sulfochlorides, which is entirely understandable if one takes into account the reversibility of reaction (1).

This is also indicated by the figures in parentheses in Table 2, which show how much the amounts of sulfochlorides decrease if, while keeping all other conditions the same, one uses $ClSO_3H$ containing dissolved hydrogen chloride (0.40 wt. %) —such an acid was obtained by passing HCl, dried over P_2O_5, into ordinary acid.

There can hardly be any doubt that the formation of sulfones during sulfonation with oleum under ordinary conditions proceeds according to the same principle as with $ClSO_3H$.* The amounts of sulfones here are much smaller (^{4}) than in the sulfonation of the same compounds with $ClSO_3H$, owing to the fact that, in their sulfonating action, the mixed anhydrides are weak competitors of oleum: one may assume, for example, that $2,5\text{-}Cl_2C_6H_3SO_2 \cdot OSO_2OH$ sulfonates 1,4-dichlorobenzene only very slowly at 20°.

Let us examine scheme (2) in more detail. It is known (^{5}) that sometimes, in the preparation of sulfochlorides, $ClSO_3H$ is partially replaced by oleum. We sulfochlorinated a series of substances with a mixture of $ClSO_3H$ and oleum, and became convinced that, for complete formation of sulfochlorides, with the ratio of sulfonating agents taken, minutes are required, not hours, as follows from the data of Table 1. We give here only the experiments with 1,4-dichlorobenzene. The finely ground substance (0.02 mol) is introduced over the course of 2 min into a mixture of $ClSO_3H$ (0.10 mol) and 60% oleum (0.03 mol SO_3), cooled to 0°; the mass warms to 20—22° and the dichlorobenzene dissolves; after 10 min it is poured onto ice. Along with the sulfonic acid, sulfochloride is obtained, 54% of theory. If, conducting the process in exactly the same way, the temperature is not allowed to rise above 1—2°, the anhydride of the sulfonic acid precipitates, the amount of which after 10 min of stirring is about 45% of theory; even when the temperature is raised to 20—25°, the anhydride only slowly goes into solution; 1,4-dibromobenzene behaves almost the same way.

We imagine that 1,4-dichlorobenzene, on being sulfonated with oleum, is converted into the sulfonic acid, part of which, under the influence of an excess of pyrosulfuric acid (or SO_3), by virtue of equilibrium (4), is obtained in the form of the mixed anhydride; the latter reacts rapidly both with $ClSO_3H$, forming sulfochloride, and with the sulfonic acid, forming the anhydride of the sulfonic acid (see below), which in turn then passes into the sulfochloroseries. When the temperature is lowered, formation of the sulfochloride is slowed, and the sparingly soluble anhydride crystallizes as it accumulates.

As for the reverse course of reaction (2), we report the following. With excess oleum, sulfochlorides react much more rapidly than with monohydrate: if a finely ground substance (0.01 mole) is stirred for the time indicated below at 20° with 8.0 ml of 20% oleum, after which the mixture is poured onto ice, then the amount of remaining sulfochlorides is expressed by the following values (%):

Substance	Time	Remaining sulfochloride, %
Benzenesulfochloride	2 min.	13.7
4-Chlorobenzenesulfochloride	5 min.	12.0
2,5-Dichlorobenzenesulfochloride	20 min.	12.0
2,4,5-Trichlorobenzenesulfochloride	40 min.	14
2,3,4,6-Tetrachlorobenzenesulfochloride	120 min.	5
3-Nitrobenzenesulfochloride	120 min.	16.7

The action of 100% H_2SO_4 under identical conditions is noticeable only on benzenesulfochloride, which is regenerated in an amount of about 96% of that taken.

It is known (^{4}) that, upon sulfonation of many halogen-substituted benzenes with large excesses of oleum, sulfonic acid anhydrides are obtained. The process of formation of the latter undoubtedly proceeds through the stage of mixed anhydrides according to scheme (4), reading it from right to left. It goes without saying that mixed anhydrides are also formed by direct addition of SO_3 to molecules of sulfonic acids. The mixed anhydrides, on further interaction with sulfonic acids, are converted into sulfonic acid anhydrides:

$$\mathrm{ArSO_2 \cdot O \cdot SO_2OH + ArSO_3H \rightleftarrows ArSO_2 \cdot O \cdot SO_2Ar + H_2SO_4}. \qquad (5)$$

In a number of cases the formation of sulfonic acid anhydrides does not occur because of their too great solubility in H_2SO_4; equilibrium (5) is shifted strongly to the left. We have established that if the anhydrides of these sulfonic acids (for example, 4-chlorobenzene- or 3,4-dichlorobenzenesulfonic acids) are dissolved in a small amount of 20% oleum, then on cooling they partially crystallize from the thick syrupy mass. On the other hand, the anhydrides of such sulfonic acids can readily be obtained if, during sulfonation, the amount of solvent is reduced; thus, for example, when unsymmetrical tetrachlorobenzene (0.01 mole) is treated with 60% oleum (0.03 mole SO_3) at 20°, the yield of the corresponding anhydride exceeds 50% of theory.

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* Such a view was recently expressed in the study of the action of SO_3 on benzene (^{6}).

In accordance with the foregoing, it should be considered that, in sulfonation with oleum of low or moderate concentration under mild temperature conditions (when the content of free SO_3 in the mixture is relatively small), the principal sulfonating agent is the incomplete anhydride of sulfuric acid—pyrosulfuric acid.

S. A. Sobchinskaya took part in the experimental part of the work.

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