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Sulphation Of N-Alkyl Anilines With Oleum

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ABSTRACT

In this article, we can conclude that oleum with a high content of sulfur dioxide should be used for sulfation to increase the content of practically valuable m-isomers in mixtures. However, oleum containing 33-54% free SO3 is practically unsuitable for sulfonation due to its high crystallization temperature. In addition, high resin content has been reported in oleum containing over 50% free SO3 when mixed with H-alkylanilines.

KEYWORDS

N-Alkylanilines, Sulfonation, Sulfonation Mixtures, M-Isomers, Mercaptan, Oltingugurt, Claus.

INTRODUCTION

Sulfonic acids of H-alkylanilines are used as intermediates in the preparation of dyes. The process of sulfonation of N-alkylanilines at high temperatures, leading to the production of n-isomers, has been studied in great detail. The sulfonation of N-alkylanilines with oleum at moderate temperatures has been studied in less detail. It is known from the literature that sulfonation of H-alkylanilines with oleum results in a mixture of p- and m-isomeric aminosulfonic acids [1]. However, their ratio in sulfonation mixtures is not precisely defined. It is also not known whether o-isomers are formed upon sulfonation of H-alkylanilines with oleum.

In the present study, the processes of sulfonation of H-alkylanilines and sulfates of H-

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alkylanilines with oleum with different contents of free anhydride were studied.

Table 1 shows the results of studying the isomeric composition of sulfonated mixtures formed upon sulfonation of H-alkylanilines with 30.1% oleum.

As can be seen from the data in the table. 1, upon sulfonation, all three isomeric sulfonic acids are formed. In this case, the content of m-isomers in the reaction mixtures decreases with a decrease in the amount of oleum taken for sulfonation and increases with an increase in the basicity of n-alkylaniline. The temperature and duration of the reaction do not significantly affect the isomeric composition of sulfonation mixtures, which indicates the absence of sulfonation isomerization of sulfonic acids and the irreversibility of the sulfonation reaction under these conditions[1].

In the study of sulfonation of tertiary amines of the benzene series, it was shown that the isomeric composition of sulfonated mixtures is greatly influenced by the acidity of the sulfonating agent [2]. With an increase in its acidity, the content of m-isomers in sulfo-mixtures increases and the number of and m-isomers decreases. These changes are explained by the simultaneous sulfonation of the protonated and non-protonated forms of amines in equilibrium.

Table 1

Sulfonation of n-alkylanilines with 30.5% oleum

N-Alkylaniline	Temperature (°C)	Duration (ч)	Moles taken SO_2 per mole n-alkylaniline	Isomeric composition of sulfonated mixtures (wt%) *		Remaining N-alkylaniline (% of taken)
				орто	мета	
N-Methylaniline	20	2	3,03	3,8	55,2	0,5
	40	1	3,04	3,7	25,2	0,7
	40	2	3,04	3,5	55,1	0
	40	4	2,56	3,9	54,6	0,9
	60	10	2,09	4,0	54,2	2,3
	60	1	3,02	3,8	55,0	0
	80	3	2,55	3,4	54,6	0
	80	5	3,05	3,9	54,9	0
	100	1	2,10	3,4	54,1	1,2

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N-ethylaniline	20	4	3,01	3,0	54,8	0,6
	40	1	3,02	2,8	63,8	1,2
	40	2	3,03	2,7	63,7	0,5
	60	1	3,04	2,5	63,6	0
	60	10	2,55	3,1	63,6	1,6
	60	10	2,11	3,0	63,0	9,7
	80	1	3,02	2,9	62,7	0
	100	1	3,03	2,6	63,5	0
	100	3	2,56	2,9	63,5	0
	100	4	2,10	3,2	63,1	4,6
N-Isopropylaniline	20	10	3,04	1,8	66,1	2,7
	40	10	3,02	1,7	66,1	0,8
	60	3	3,03	1,8	65,6	3,8
	60	5	2,55	1,5	65,5	2,1
	60	10	2,55	1,9	66,0	0
	80	3	3,03	1,6	65,8	0
	100	3	3,05	1,7	65,6	3,0
	100	10	2,11			

The content of the n-isomer in sulfonation mixtures is easy to calculate, since the total content of the three isomers is 100% During sulfonation of H-alkylanilines, apparently, similar regularities should be observed, which is confirmed by changes in the composition of the reaction mixtures depending on the amount of oleum taken and the basicity of H-alkylaniline[3].

This is also confirmed by the experiments carried out on the sulfonation of H-alkylanilines with oleums with different contents of free sulfuric anhydride. Shown in

Fig. 1, the dependence of the content of m-isomers in the resulting mixtures on the acidity function of oleums shows that the isomeric composition of sulfonation mixtures strongly depends on the acidity of the sulfonating agent. With an increase in its acidity in sulfonated mixtures, the content of and n-isomers decreases and the amount of the m-isomer increases, which confirms the fact of sulfonation of protonated and non-protonated forms of N-alkylanilines in equilibrium [4].

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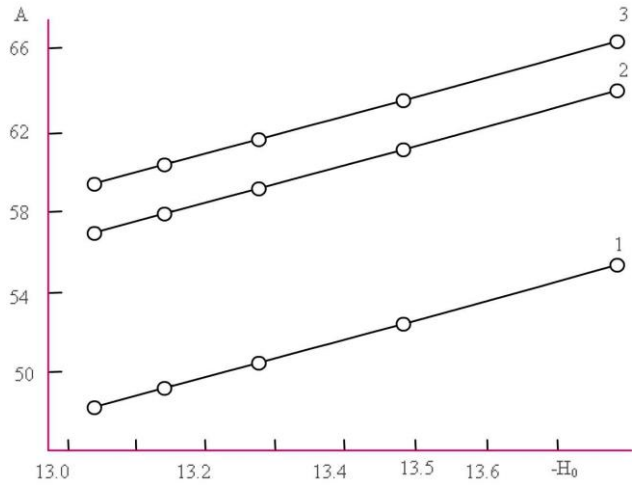

Rice. 1. Dependences of the content of m-isomers A (%) in the resulting mixtures on the acidity function of oleum (- H_0) during sulfonation of H-methylaniline (1), H-etplaniline (2) - H-isopropylaniline (3).

The data given in table. 1 and fig. 1, allow us to conclude that in order to increase the content of practically valuable m-isomers in mixtures, oleums with a high sulfuric anhydride content should be used for sulfonation. However, oleums containing 33-54% free SO_3 are practically unsuitable for sulfonation due to their high crystallization temperatures. In addition, oleums with a free SO_3 content of more than 50%, already at the moment of mixing with H-alkylanilines, strongly resinify the latter. It was possible to increase the concentration of sulfonating oleum by sulfonating N-alkylaniline sulfates [5].
The results of studying the sulfonation of sulfates of N-alkylanilines of N-alkylanilines with 61.4% oleum are presented in Table 2.

From the data table. 2 that the content of m-isomers in sulfonation mixtures obtained by sulfonation of H-alkylanilines with 61.9% oleum is 13-15% higher than in mixtures formed upon sulfonation with 30.1% oleum. The content of the m-isomer in the mixtures slightly increases with an increase in the amount of oleum taken for sulfonation [6].

To elucidate the mechanism of sulfonation of N-alkylanilines with oleum, the kinetics of this reaction was studied. To avoid the release of heat during mixing of the components, sulfates of N-alkylanilines were used for sulfonation. We studied the kinetics of sulfonation of H-alkylaniline sulfates with oleum with a free SO_3 content of 10, 12.5, 16, 21.5% at a weight ratio of sulfonating oleum to H-alkylaniline sulfates equal to 150: 1.

The kinetic processing of the obtained experimental data showed the first order of the reaction with respect to the organic component [7]. The average values of the effective rate constants of the reaction of sulfonation of sulfates of N-alkylanilines, calculated by the method of least squares, are presented in table. 3. From the data table. 3

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that the values of the effective rate constants regularly increase with an increase in the concentration of SO_3 in oleum and a decrease in the basicity of H-alkylaniline.

Table 2

Sulfonation of N-alkylaniline sulfates with 61.9% oleum

N-Alkylaniline	Temperature (°C)	Duration (h)	Taken moles of SO_2 per 1 mole of N-alkylaniline	Isomeric composition of sulfonated mixtures (wt%) *		Remaining N-alkylaniline (% of taken)
				орто	мета	
N-Methylaniline	20	2	4,75	2,5	70,2	2,7
	20	4	4,76	2,7	69,2	0,8
	40	2	4,76	2,7	69,1	1,0
	40	4	3,23	3,2	68,6	0
	50	1	4,09	2,8	69,2	0,6
	50	2	4,75	3,0	69,0	0
	50	2	4,22	3,2	69,6	1,6
	50	3	4,24	3,0	76,9	0
N-ethylaniline	20	5	5,92	2,1	76,1	1,2
	40	2	5,91	1,8	776	1,4
	40	2	5,01	3,0	54,8	0,6
	40	4	5,09	2,8	63,8	1,2
	40	5	5,93	2,7	63,7	0,5
	60	1	5,04	2,5	63,6	0
	60	2	5,55	3,1	63,6	1,6
	60	3	5,11	3,0	63,0	9,7
N-Isopropylaniline	40	4	7,02	1,8	66,1	2,7
	40	6	7,03	1,7	66,1	0,8
	40	10	6,56	1,8	65,6	3,8
	60	2	7,10	1,5	65,5	2,1
	60	3	7,12	1,9	66,0	0
	60	3	6,41	1,6	65,8	0
	60	5	7,12	1,7	65,6	3,0

The activation energies of the sulfonation reaction of H-alkylanilines change little with an increase in the SO_3 concentration in oleum and an increase in the size of the H-alkyl substituent (Table 4). This indicates the identity of the reaction mechanisms during sulfonation of H-alkylanilines of various structures.

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Table 3

Effective rate constants (k_{eff}) of the reaction of sulfonation of sulfates of N-alkyl-anilines with oleum of various concentrations

Temperature. (°C)	Oleum concentration (% free SO2)	*The quantities k_{eff} .10(c^{-1}) sulfonation reactions sulfates*		
		N-methylaniline	N-ethylaniline	N-isopropylaniline
7 , 6	10,0	0,447	0,362	0,291
19,4	10,0	1,23	1,01	0,813
31,1	10,0	3,13	2,58	2,08
7,6	12,5	0,703	0,581	0,455
19,4	12,5	1,95	1,62	1,29
31,1	125	5,00	4,15	3,34
7,6	16,0	1,34	1,13	0,860
19,4	16,0	3,72	3,16	2,46
31,1	16,0	9,52	8,09	6,41
7,6	21,5	2,91	2,43	1,93
12,9	21,5	4,67	3,92	3,12
19,4	21,5	8,13	6,92	5,50

Table 4

Values of activation energies E of the reaction of sulfonation of sulfates of N-alkylanilines with oleum

Concentration oleum (% free SO2)	*The quantities $k_{эфф}$.10(c^{-1}) sulfonation reactions of sulfates*		
	N-methylaniline	N-ethylaniline	N-isopropylaniline
10,0	58,7	59,5	59,5
12,5	59,1	59,5	60,3
16,0	59,1	59,9	60,8
21,5	59,5	60,8	60,8

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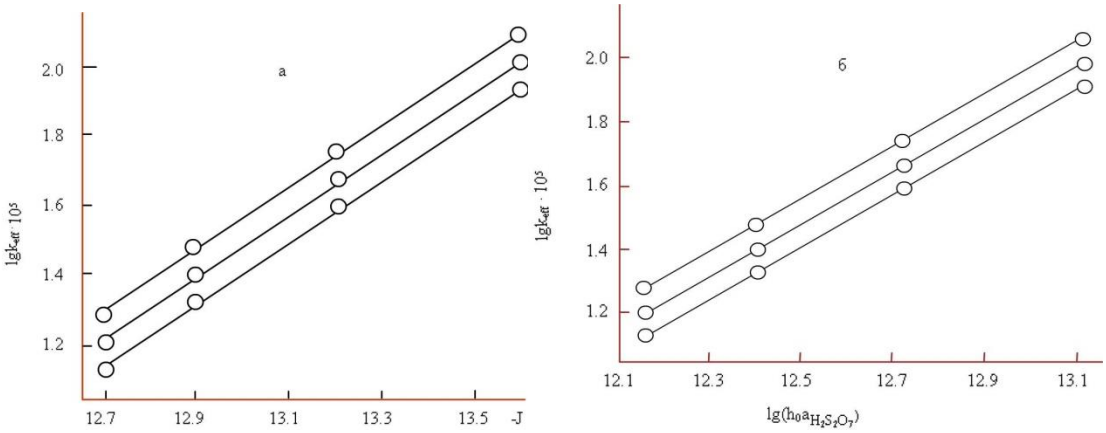
In fig. 2 shows the dependences of the logarithms of the effective rate constants of the sulfonation reaction of sulfates of H-alkylanilines, reduced to a temperature of 25 °, in oleums of various concentrations on the function J = H_0 - log pSO_3 [8] (where Ho is a function of oleum acidity, pSO_3 is the partial vapor pressure over oleums) and from log ($AH_2S_2O_7$ .ho) (where a $H_2S_2O_7$ is the activity of $H_2S_2O_7$, h_0 is the Hammett acidity of oleum).

The values of the acidity function of oleums H_0 and acidity h_0 were taken from the literature, and the partial pressures of SO_3 over the oleums were calculated from the literature data using the Cliperon-Clausius equation. The values of $H_2S_2O_7$ are taken from the literature [9].

As can be seen from Fig. 2, the values of logkeff correlate well with both the J-function of oleums and the values of log ($aH_2S_2O_7$), and the slopes of the straight lines are ≈1. Since the partial pressures of SO_3 over oleums pSO_3 are proportional to the activities of sulfuric anhydride in oleums aSO_3 [5], a good correlation of logkeff with the J-function of oleums suggests that the sulfonating particle in oleums is the HSO_3 + ion, which is consistent with the literature data [10]. However, a good correlation with the values of log ($aH_2S_2O_7$ .ho) allows us to make the assumption that the sulfonating particle can be an ion $H_2S_2O_7$ + that



Rice. 2. Dependences of the logarithms of the effective rate constants lg keff of sulfonation of H-alkylanilines at 25 ° on the J-function of oleums (a) and on the value of log (h_0 • $H_2S_2O_7$ +) 1 - H-methyl aniline, 2 - H-ethylaniline, 3 - H- isopropylaniline.

Literary data also confirm [11]. Thus, by the kinetic method, due to the constancy of the thermodynamic activity of sulfuric acid in dilute oleum, it is impossible to distinguish between sulfonation mechanisms with the participation of H_2SO_3 + and $H_2S_2O_7$ + ions.

The obtained kinetic data allow us to conclude that, upon sulfonation of H-alkylanilines with oleum, the composition of the transition state includes an unprotonated or protonated H-alkylaniline molecule, a sulfuric anhydride molecule, a proton, and, possibly, a sulfuric acid molecule.

Experimental Part

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Sulfonation of H-alkylanilines and their sulfates, as well as the study of the kinetics of sulfonation of sulfates of H-alkylanilines with oleums was carried out according to the methods described earlier. Analysis of reaction mixtures for the content of isomeric H-alkylaniline sulfonic acids and unreacted H-alkylanilines in them was carried out by spectrophotometric and bromometric methods similar to those described earlier.

We used pure H-alkylanilines. The composition of oleums was determined by electrical conductivity, as well as by the volumetric method. Sulfates of H-alkylanilines were obtained and purified by methods described in the literature.

CONCLUSIONS

1. Studies of the sulfonation of H-alkylanilines and sulfates of H-alkylanilines with oleum of various concentrations showed that the isomeric composition of the resulting sulfonation mixtures changes depending on the acidity of the sulfonating agent and the basicity of the H-alkylaniline. This indicates the occurrence of the sulfonation reaction with both the protonated and the non-protonated form of H-alkylaniline in equilibrium with it, the proportion of which varies with the acidity of the medium.
2. The study of the kinetics of sulfonation of H-alkylaniline sulfates with oleums of various concentrations showed that the sulfonating particle in oleums can be HSO_3 + or and $H_2S_2O_7$ + ions. The transition state consists of a non-protonated or protonated H-alkylaniline molecule, a sulfuric anhydride molecule, a proton, and possibly a sulfuric acid molecule.

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