



## تكوين حمض الأنيلين أحادي السلفونيك

خليفة عبدالسلام الفلوس<sup>1</sup> ، إسماعيل عبدالسلام هيبلو<sup>2</sup>

قسم الكيمياء ، كلية العلوم ، الجامعة الأسمرية الإسلامية ، زليتن ، ليبيا

[k.alfallos.asmsrya@edu.ly](mailto:k.alfallos.asmsrya@edu.ly)

## FORMATION OF ANILINE MONOSULPHONIC ACID

<sup>1</sup> Khalifa A. Alfallous, <sup>2</sup> Ismail A. Heblow

Department of Chemistry, Faculty of Science ,Alasmarya Islamic University, Zliten, Libya <sup>1,2</sup>

تاريخ الاستلام: 2024-07-30 تاريخ القبول: 2024-08-16 تاريخ النشر: 2024-09-04

### الملخص:

تعتبر دراسة سلفنة الأنيلين مهمة لتخليق البولي أنيلين مع البدائل في السلسلة الجانبية. حيث تم استخدام سلفنة كبريتات الأنيلين الأحادية المنقى مع أحادي الهيدرات والزيت. تم إجراء التحليل الكمي لأيزومرات حمض الأمينوسلفونيك باستخدام طرق القياس الطيفي والبرومتري. حيث تؤدي زيادة تركيز ثالث أكسيد الكبريت  $SO_3$  في زيت السلفنة إلى زيادة في كمية حمض الميثانيليك مقارنة بالأيزومرات الأورثو والبارا (ortho- and para- isomers) ) كما أن عملية زيادة تركيز الأيزومير ميتا ( meta-isomer ) هي دالة خطية لحموضة الزيت. كما أن إضافة حمض tetrabisulfate boric acid إلى الزيت يساعد أيضاً في زيادة إنتاج حمض الميثانيليك. وقد أظهرت مقارنة طاقات التنشيط أن حمض tetrabisulfate boric acid لم يكن له أي تأثير على آلية السلفنة وحالة الانتقال. ويقدم العمل بيانات جديدة حول آليات سلفنة الأنيلين. الكلمات الدالة: الأنيلين، أحادي الكبريتات، الطيف الضوئي، طاقة التنشيط.

### Abstract

The study of aniline sulfonation is important for the subsequent synthesis of polyaniline with substituents in the side chain. Sulfonation of purified aniline monosulfate with monohydrate and oleums was used. Quantitative analysis of aminosulfonic acid isomers was carried out using spectrophotometric and bromometric methods. An increase in the  $SO_3$  concentration in the sulfonating oleum leads to an increase in the amount of methanilic acid compared to the ortho- and para-isomers. The process of increasing the concentration of the meta-isomer is a linear function of the acidity of the oleum. The addition of tetrabisulfate boric acid to the oleum also helps to increase the yield of methanilic acid. A comparison of activation energies showed that tetrabisulfate boric acid had no effect on the sulfonation

mechanism and the transition state. The work presents new data on the mechanisms of aniline sulfonation.

**Keywords:** aniline, monosulfate, spectrophotometric, activation energies

## 1. Introduction:

Aniline monosulphonic acid is formed by the action of oily sulphuric acid on aniline, and is usually prepared by boiling aniline for some time so that it dissolves in the sulphuric acid. The solution darkens at first and then deposits crystals of aniline monosulphonic acid. The reaction is therefore used in the manufacture of aniline monosulphonic acid. The attention given to the formation of aniline monosulphonic acid was based mainly on the fact that several sulphonic derivatives of aniline are used in the dye industry. The preparation of m-aminophenol and of p-aminophenol from aniline with a creamy heat-activated sulphate was investigated by Muschiolik, but the formation of aniline-monosulphonic acid was not mentioned on that occasion. However, it seems that period heat-activated sulphates in which aniline monosulphonic acid is the main product have not been previously studied. Aniline is an amine. The substitution of one hydrogen atom of NH<sub>2</sub> group with a monosulfonic acid radical forms monosulfonic acid by aromatic amine. Aniline monosulfonic acid is derived from the reaction of aniline and dilute sulphonation with sulfuric acid, which controls the reactivity into the ortho position. By this method, the introduction of a second sulfonate in the ortho position and other positions is very difficult. The degree of control is set by the dilute condition. Generally, the term "aniline monosulfonic acid" is used to describe the final product directly after the sulphonation without completing the purification, which monosulfonic content is within the range of 65-70%. However, for some applications, 75-85% monosulfonic content level aniline monosulfonic acid is desired.

Aniline monosulfonic acid is an important organic intermediate and compound of 3 chemical industries, i.e., pharmaceutical industry, dye industry, and pesticide and rubber processing auxiliary industry, etc. Its wide application makes it having good developing potential in chemical industry. In biochemistry, aniline monosulfonic acid can be used to synthesize calmodulin chloride, and can also be used as an antagonist of N-methyl-D-aspartate receptors. In dye industry, sulphonating aniline into aniline monosulfonic acid is the initial and crucial step in sulphonating disperse dyes. In pharmaceutical industry, the main variety of the downstream products of aniline monosulfonic acid is  $\alpha$ -phenylethylamine, which has an annual demand of about 5,000 - 10,000 tons worldwide.

A polymer compound that attracts the attention of researchers is polyaniline. This is due to the presence of a system of conjugated p- or r-bonds in polyaniline, which gives it electrical conductivity properties. The ease of synthesis and stability, along with useful physicochemical properties, make polyaniline an important chemical product [1]. At the same time, poor solubility and refractoriness of

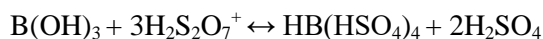
polyaniline limit its use. The solubility of polyaniline can be increased by including side functional groups [2], including through the use of aniline monosulfonic acids.

The isomeric composition of sulfonic mixtures during sulfonation of aniline sulfate with oleum under different conditions varies depending on the acidity of the sulfonating agent; When sulfonated with oleum containing tetrabisulfate boric acid, sulfonate mixtures with a high content of methanilic acid are formed. The rate of sulfonation increases with increasing acidity of the sulfonating agent, which confirms the sulfonation mechanism with the participation of  $\text{HSO}_3^+$  and  $\text{H}_3\text{S}_2\text{O}_7^+$  ions as electrophiles. Aniline sulfonic acids are important intermediates in the production of dyes. The sulfonation of aniline at high temperatures ( $\sim 180^\circ\text{C}$ ), leading to the production of sulfanilic acid, has been studied in some detail. The process of sulfonation of aniline at moderate temperatures ( $20\text{-}100^\circ\text{C}$ ) has been studied less thoroughly, despite the fact that this is the simplest way to obtain methanilic acid, which is a practically valuable intermediate compound. It is known from the literature that when aniline sulfate is sulfonated with oleum, a mixture of three isomeric monosulfonic acids is formed, and the ratio of the content of the meta-isomer to the content of ortho- and para-isomers in the resulting sulfonic mixtures is always less than one [3]. The low content of methanilic acid in the resulting sulfonic acid mixtures is apparently the reason that the industrial method for producing this aminosulfonic acid is based on the sulfonation of nitrobenzene with oleum, followed by the reduction of m-nitrobenzenesulfonic acid to methanilic acid.

## 2. Experimental:

Due to the strong tarring of reaction mixtures during sulfonation of aniline base with oleum, aniline sulfate purified by the method described in [8] was used in this work. The sulfonation of aniline sulfate and the study of the kinetics of sulfonation with monohydrate and oleums with different contents of tetrabisulfateboric acid were carried out according to the methods of [4]. The analysis of reaction mixtures for the content of isomeric aminosulfonic acids and unreacted aniline was carried out spectrophotometrically and bromometrically.

Solutions of tetrabisulfateboric acid in oleums and monohydrate were prepared by reacting boric acid with oleum of appropriate concentration according to the equation:



The values of the acidity function of oleums and monohydrate containing tetrabisulfateboric acid are taken from [6].

## 3. Result and discussion:

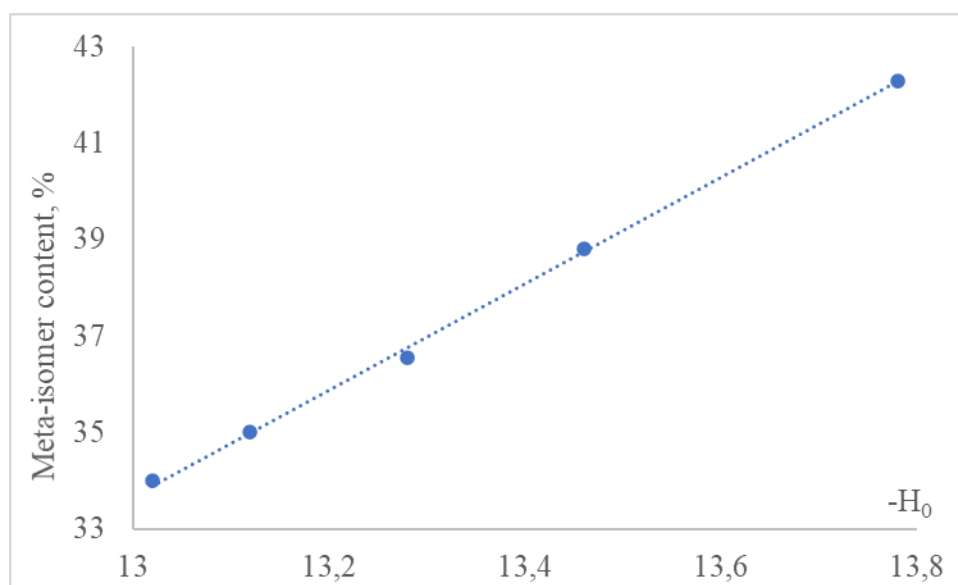
In this study, the sulfonation of aniline sulfate with oleum was studied in order to find optimal conditions for the production of methanilic acid. As can be seen from the data in Table 1, with an increase in the concentration of free  $\text{SO}_3$  in the sulfonating oleum, the content of methanilic acid in the resulting sulfonate mixtures increases. An increase in the amount of oleum taken for sulfonation also leads to a slight increase in the content of methanilic acid. The resulting sulfonic mixtures contain over 50%

sulfanilic acid. The amount of orthanilic acid is also higher than the content of ortho isomers in sulfonate mixtures formed during the sulfonation of tertiary amines of the benzene series [4].

**Table 1. Sulfonation of aniline sulfate with oleum**

Content of free SO <sub>3</sub> in oleum, wt%	Temperature, °C	Reaction duration, h	Weight ratio of oleum to aniline sulfate	Taken moles of SO <sub>3</sub> per mole of aniline sulfate	Isomeric composition of sulfonic mixtures, wt%			Residue of aniline sulfate to the introduced one, %
					ortho-	para-	meta-	
100 _	80	5	7.01	2.53	5.7	61.1	33.2	3.8
10.0	80	3	7.99	2.89	5.5	61.0	33.5	2.6
10.0	80	5	8.00	2.89	5.4	61.0	33.6	1.4
20.1	80	3	5.02	3.65	5.1	59.0	35.9	1.0
20.1	80	1	6.00	4.35	4.9	58.7	36.4	0.8
20.1	80	2	6.01	4.36	4.8	58.9	36.3	0
30.0	20	3	4.01	4.35	4.5	57.0	38.5	1.6
30.0	40	3	4.00	4.34	4.6	57.2	38.2	3.2
30.0	60	1	4.02	4.36	4.4	57.2	38.4	1.3
30.0	60	3	4.02	4.36	4.6	57.3	38.1	0.6
30.0	80	1	3.99	4.33	4.7	57.3	38.0	0.3
30.0	60	1	4.50	4.88	4.2	56.9	38.9	0.3
30.0	60	2	4.50	4.88	4.1	56.9	39.0	0
30.0	40	1	5.01	5.43	4.2	55.7	40.1	0

Changes in the composition of sulfonic mixtures depending on the concentration and amount of oleum taken are associated with changes in the acidity of the medium, which determines the number of protonated aniline molecules that undergo sulfonation along with non-protonated ones. Shown in Fig. Figure 1, the dependence of the meta-isomer content on the acidity function of oleum shows that with increasing acidity in sulfonic mixtures, the content of ortho- and para-isomers decreases and the amount of meta-isomer increases, which confirms the fact of sulfonation of the protonated and non-protonated forms of aniline, which are in equilibrium. Based on the above, we can conclude that in order to increase the content of methanilic acid in sulfonate mixtures, highly concentrated oleums should be used for sulfonation. However, the use of 60-65% oleum for sulfonation of aniline sulfate, similar to the methods for sulfonation of methylaniline [5], did not lead to positive results due to the strong oxidation of aniline.



**Figure 1. Dependence of the meta-isomer content in the resulting mixtures on the function of oleum acidity ( $-H_0$ ).**

It seemed possible to increase the content of methanilic acid in the resulting mixtures by using 30% oleum containing tetrabisulfateboric acid for sulfonation of aniline sulfate. Tetrabisulfateboric acid is not a sulfonating agent, however, it is a stronger acid compared to pyrosulfuric acid, and systems containing it have a higher acidity [6]. As can be seen from the data in Table 2, sulfonation of aniline sulfate with 30% oleum containing 5-30% tetrabisulfateboric acid can significantly increase the content of methanilic acid in sulfonate mixtures and with an increase in the amount of tetrabisulfateboric acid from 0 to 30 wt%, the content of methanilic acid increases by 16.5 -18.5 wt%.

**Table 2. Sulfonation of aniline sulfate with 30% oleum containing tetrabisulfateboric acid at 40 °C**

Reaction duration, h	Concentration of tetrabisulfateboric acid in 30% oleum, wt%	Taken moles of SO <sub>3</sub> per mole of aniline sulfate	Isomeric composition of sulfonic mixtures, wt%			Residue of aniline sulfate to the introduced one, %
			ortho-	para-	meta-	
3	5.1	4.35	4.0	54.1	41.9	0.6
1	10.2	4.34	3.7	50.4	45.9	0.5
1	15.0	4.36	3.6	47.3	49.1	0
1	19.9	4.07	3.4	44.0	52.6	1.7
1	25.1	4.06	3.2	41.1	55.7	0
2	25.1	3.64	3.3	41.8	54.9	0.6
3	25.1	3.26	3.6	42.1	54.3	1.2
1	30.2	4.06	2.3	38.9	58.8	0
1	30.2	3.65	2.6	39.8	57.6	0
2	30.2	3.25	2.7	40.5	56.8	0.7

To elucidate the mechanisms of sulfonation of aniline sulfate, the kinetics of sulfonation with monohydrate and oleums containing tetrabisulfate boric acid was studied. Since in all kinetic experiments

the mass ratio of the sulfonating agent to aniline sulfate was 150:1, the effective sulfonation rate constants were calculated using a first-order kinetic equation.

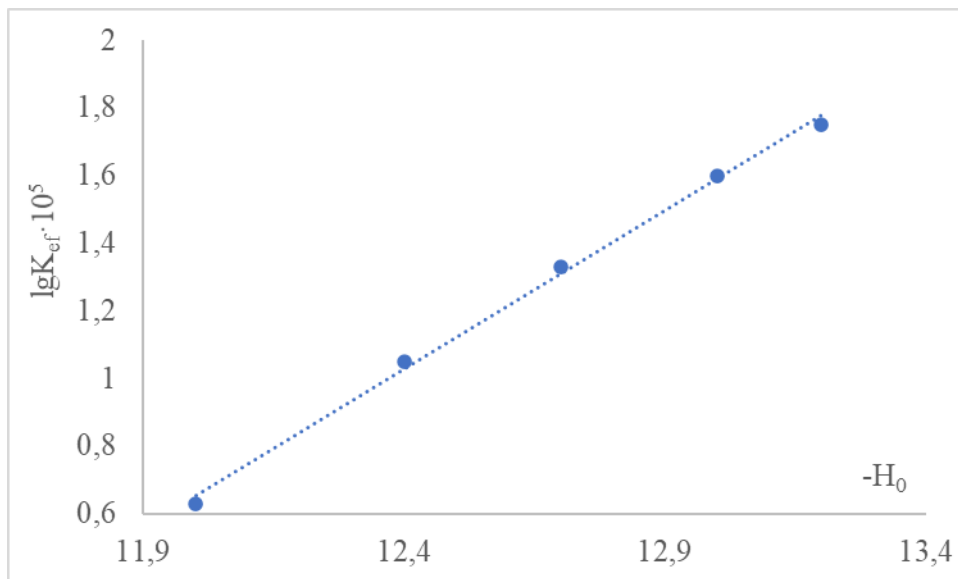
Table 3. shows the average values of the effective rate constants for the sulfonation of aniline sulfate, the activation energy and the logarithms of the pre-exponential factors, calculated by the least squares method. It can be seen that the effective rate constants of sulfonation naturally increase with increasing concentration of tetrakisulfate boric acid in the monohydrate and oleums; in this case, the effective rate constants are significantly greater than the corresponding sulfonation constants with monohydrate and oleums not containing  $\text{HB}(\text{HSO}_4)_4$ . Obviously, increasing the acidity of the sulfonating agent significantly increases the rate of sulfonation. The latter circumstance confirms the classical mechanism of sulfonation of benzene series amines with the participation of  $\text{HSO}_3^+$  and  $\text{H}_3\text{S}_2\text{O}_7^+$  ions as electrophiles [7], which is more preferable than the mechanism of sulfonation with monomeric sulfuric anhydride.

**Table 3. Values of effective rate constants of aniline sulfate monohydrate and oleums containing tetrakisulfate boric acid and parameters of the Arrhenius equation**

Reaction temperature, °C	Concentration of free $\text{SO}_3$ in the system, wt%	Concentration of tetrakisulfateboric acid, wt%	$k_{\text{ef}} \cdot 10^4$ , $\text{sec}^{-1}$	E kJ/Mol	log $B$
31.1	0	0	0.418		
31.1	0	5.0	1.21		
31.1	0	10.0	2.02		
31.1	0	20.0	3.67		
7.6	0	30.0	0.931		
19.4	0	30.0	2.28	52.0	5.63
31.1	0	30.0	5.19		
7.6	10.0	0	0.815		
7.6	10.0	10.0	3.89		
12.9	10.0	10.0	5.85	51.5	6.17
19.4	10.0	10.0	9.46		
0	10.0	20.0	3.83		
7.6	10.0	20.0	7.08	51.5	6.43
12.9	10.0	20.0	10.6		
0	10.0	30.0	5.08		
7.6	10.0	30.0	9.33	51.1	6.47
7.6	12.5	0.0	1.22		
0	12.5	10.0	3.13		
7.6	12.5	10.0	5.82	52.0	6.42
12.9	12.5	10.0	8.79		
7.6	16.0	0	2.31		
0	16.0	5.0	3.54		
7.6	16.0	5.0	6.61	52.4	6.55
12.9	16.0	5.0	10.0		

The effective rate constants of the reaction of sulfonation of aniline sulfate with monohydrate containing tetrakisulfate boric acid on the  $H_0$  function is linear (Fig. 2). The angular coefficient of the

straight line in Fig. 2 is equal to 0.94, i.e. close to unity. This also confirms the sulfonation mechanism with the participation of  $\text{HSO}_3^+$  and  $\text{H}_3\text{S}_2\text{O}_7^+$  ions, which are proton carriers.



**Figure 2. Dependence of the logarithms of effective rate constants for sulfonation of aniline sulfate ( $\log K_{\text{ef}}$ ) on the acidity function of the monohydrate containing tetrabisulfateboric acid ( $-H_0$ ); temperature 31.1 °C.**

A comparison of the activation energies given in Table 3 with the activation energies obtained during sulfonation of aniline sulfate with oleums not containing tetrabisulfateboric acid allows us to conclude that the introduction of tetrabisulfateboric acid into oleums does not have a noticeable effect on the values of activation energies and does not change the mechanism of sulfonation of aniline sulfate and the structure of the transition state.

As can be seen from the data in Table 4, the effective rate constants for the formation of ortho-, para- and meta-isomers increase with increasing concentration of tetrabisulfateboric acid in the monohydrate and oleums.

**Table 4. Values of effective rate constants for the formation of ortho-, para- and meta-isomers during sulfonation of aniline sulfate with monohydrate and oleums containing tetrabisulfateboric acid**

Reaction temperature, °C	Concentration of free $\text{SO}_3$ in the system, wt%	Concentration of tetrabisulfateboric acid, wt%	$k_{\text{ef}}^{\text{ortho}} \cdot 10^5, \text{sec}^{-1}$	$k_{\text{ef}}^{\text{para}} \cdot 10^4, \text{sec}^{-1}$	$k_{\text{ef}}^{\text{meta}} \cdot 10^4, \text{sec}^{-1}$
31.1	0	0	0.297	0.279	0.109
31.1	0	5.0	0.787	0.800	0.331
31.1	0	10.0	1.25	1.31	0.582
31.1	0	20.0	2.20	2.29	1.16
7.6	0	30.0	0.540	0.557	0.320
19.4	0	30.0	1.30	1.37	0.782
31.1	0	30.0	2.96	3.12	1.77
7.6	10.0	0	0.416	0.497	0.276

7.6	10.0	10.0	1.79	2.28	1.43
12.9	10.0	10.0	2.63	3.44	2.15
19.4	10.0	10.0	4.18	5.58	3.46
0	10.0	20.0	1.61	2.16	1.51
7.6	10.0	20.0	2.97	3.99	2.79
12.9	10.0	20.0	4.33	5.99	4.18
0	10.0	30.0	2.03	2.73	2.15
7.6	10.0	30.0	3.62	5.02	3.95
7.6	12.5	0.0	0.561	0.738	0.426
0	12.5	10.0	1.31	1.79	1.21
7.6	12.5	10.0	2.39	3.33	2.25
12.9	12.5	10.0	3.60	5.04	3.39
7.6	16.0	0	0.957	1.37	0.841
0	16.0	5.0	1.31	2.07	1.34
7.6	16.0	5.0	2.31	3.88	2.50
12.9	16.0	5.0	3.60	5.87	3.77

Obviously, during the sulfonation of aniline sulfate, an increase in the acidity of the sulfonating agent increases the rate of sulfonation of unprotonated and protonated aniline molecules that are in equilibrium. This confirms the above considerations about the mechanism of sulfonation of benzene series amines with the participation of  $\text{HSO}_3^+$  and  $\text{H}_3\text{S}_2\text{O}_7^+$  ions as electrophiles.

#### REFERENCES

1. Ratheesh, R., & Viswanathan, K. (2014). Chemical polymerization of aniline using para-toluene sulphonic acid. *IOSR J. Appl. Phy*, 6(1), 1-9
2. Xu, Y., Dai, L., Chen, J., Gal, J. Y., & Wu, H. (2007). Synthesis and characterization of aniline and aniline-o-sulfonic acid copolymers. *European polymer journal*, 43(5), 2072-2079
3. Heywood, A., Mathias, A., & Williams, A. E. (1970). Identification of sulfonic acids and sulfonates by mass spectrometry. *Analytical Chemistry*, 42 (11), 1272-1273
4. Lisk, G. F. (1950). Sulfonation. *Industrial & Engineering Chemistry*, 42 (9), 1746-1760
5. Kanetani, F., & Yamaguchi, H. (1978). Studies of Reactions of Amines with Sulfur Trioxide. V. Transsulfonation of Amine Salts of Some N-Substituted Amidosulfuric Acids. *Bulletin of the Chemical Society of Japan*, 51 (10), 3039-3046
6. Gillespie, R. J., Peel, T. E., & Robinson, E. A. (1971). Hammett acidity function for some super acid systems. I. Systems  $\text{H}_2\text{SO}_4\text{-SO}_3$ ,  $\text{H}_2\text{SO}_4\text{-HSO}_3\text{F}$ ,  $\text{H}_2\text{SO}_4\text{-HSO}_3\text{Cl}$ , and  $\text{H}_2\text{SO}_4\text{-HB}(\text{HSO}_4)$  4. *Journal of the American Chemical Society*, 93 (20), 5083-5087
7. Maarsen, P. K., & Cerfontain, H. (1977). Aromatic sulphonation. Part 59. Sulphonation of aniline in concentrated aqueous and fuming sulfuric acid. *Journal of the Chemical Society, Perkin Transactions 2*, (8), 1008-1010
8. Elliot R. Alexander. Mechanism of the Sulfonation of Aromatic Amines. I. Sulfonation with Fuming Sulfuric Acid. *Journal of the American Chemical Society* 1946, 68, 6, 969-973