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Naphthalenedisulphonic Acid Formation with 20% Oleum

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Abstract:

Many authors have described naphthalene disulphonic acid formation by sulphonation of naphthalene with sulphuric acid: the proportions of the different isomers in this reaction are discussed under several sets of experimental conditions. On the contrary, little data is available concerning the use of oleum as a sulphonation medium. The use of oleum as a sulphonating medium is interesting from an industrial point of view for monosulphonic acid preparation, since it results in fast reaction rates and yields a minimum of water. However, since polysulphonic acid formation is enhanced in this way, it is important to know how much of these unwanted products are formed. The proportion of the different isomers of the obtained naphthalenedisulphonic acids is strongly dependent on reaction conditions. This work deals with the influence of reaction time and temperature on the reaction yields. HPLC is used for diacid separation and determination.

1. Introduction

The aim of this work is to compare 20% oleum naphthalene sulphonation with similar techniques proposed by several other authors using sulphuric acid[1–4] or oleum[5,6] under other conditions. The presence of oleum leads to more diacid formation than the use of sulfuric acid.[7] Initially diacids were identified by characteristic salt precipitation and subsequent separation. Although this separation works well on some isomers of naphthalenedisulphonic acids, especially those showing high symmetry, some isomers could not be separated in this way.[8] In our work, we developed a HPLC technique leading to satisfactory separation of all isomers present.

Two working temperatures have been chosen, respectively 393 and 433 K, in order to investigate the differences due to kinetically and thermodynamically controlled reactions.

Naphthalene sulphonation always leads to complex mixtures, containing several classes of products such as naphthalenemono-, -di, and -trisulphonic acids and several other more or less complex compounds.[9] Thus, we first tried to examine the specific behaviour of oleum-containing sulphonation media with naphthalene from the point of view of disulphonic acid formation.

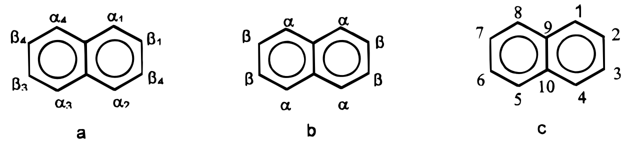

Figure 1. **Different systems for naming naphthalenes.**

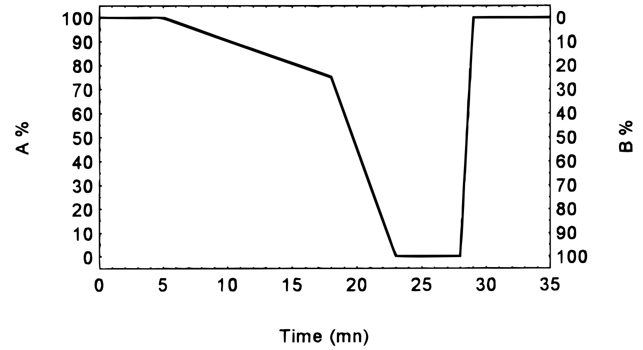

Figure 2. **Gradient used in HPLC at 333 K.**

Several systems are used[10] to define the names of naphthalenedisulphonic acids. We shall use system c (Figure 1) in the following text.

At temperatures $T < 263$ K, the main product is 1-monosulphonic acid, which is the kinetic product, and at temperatures $T > 420$ K, the main product is 2-monosulphonic acid, which is the thermodynamically most stable one.[11]

At room temperature, naphthalene sulphonation is essentially a kinetically controlled reaction, leading mainly to monosulphonic acid formation. The ratio between the monosulphonic 1- and 2-isomers increases at 298 K from 4.3 to 5.9 as sulphuric acid concentration increases from 75 to 95% in the sulphonation mixture.[11]

Disulphonic acids can be formed from monosulphonic acids. De Wit and al.[12] studied the sulphonation of 1-monosulphonic acid by a low concentration (0.25 $\text{mol}\cdot\text{L}^{-1}$) of 98.5% sulphuric acid at 298 K. Their reaction leads to 1,5-, 1,6-, and 1,7-naphthalenedisulphonic acids with respective yields of 58, 32, and 12%. Under the same working conditions, sulphonation of 2-naphthalenemonosulphonic acid leads to the 1,3-, 1,6-, and 1,7-disulphonic acids with respective yields of 4, 74, and 18%. Simultaneously, one can observe the formation of 4% of 2,6- and 2,7- disulphonic acids.

The method for the determination of 2,6- and 2,7-disulphonic acids by means of the solubility of the mixture of the lead salts cannot be used for the analysis of the

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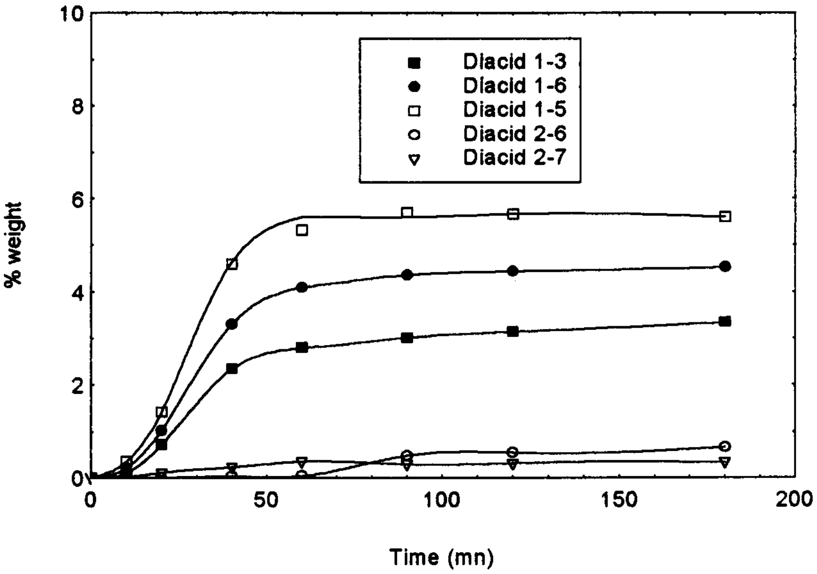

Figure 3. **Diacid concentration versus time at 393 K (weight percent related to initial total mass).**

sulfonation mixture.[13] The method for the determination of the 1,5- and 2,6-isomers as barium and lead salts has not been worked out:[14] their salts, presenting symmetric substitution, show very similar properties, leading to identical solubility behavior. The methods for determination of naphthalene-1,5-disulphonic acid by means of its *m*-xylidine salt and of the 1,6-acid as the 1-naphthylamine salt can be checked on in the absence of the 1,7-isomer,[15] which is always present in the sulphonation mixture.

The problem was to find a quick and easy method which could be used for the good determination of the different disulphonic acid isomers, in sulphonation mixtures obtained at 393 K and at 433 K.

2. Experimental Section

The reactions are carried out in a Mettler RC1 calorimeter reactor. Pure naphthalene (640 g) is heated up to the working temperature; 616 g of 20% oleum at room temperature ($T =$ 293 K) is then slowly added over 90 min (molar ratio $SO_3/C_{10}H_8 = 1.31$).

During this time, strong stirring is used in order to get the best possible homogeneity of the reacting mixtures.[16] While oleum is introduced into the mixture, the regulating system of the calorimeter keeps the temperature constant within ±0.1 K.

In order to study the kinetics of the reaction, the samples are quenched as follows: the sample (1 g) at reaction temperature is poured into cold methanol (100 mL) so that its temperature falls down below 273 K within less than 30 s. The strong dilution obtained in this way as well as the very fast drop in temperature immediately blocks all bimolecular reactions.

The characterization and the determination of the compounds present in the mixture were carried out by means of inverse phase HPLC, associating a Spectra Physics SP 8800 pump to a Lichrosorb column (RP 8, 5 μ, 250 × 4.6 mm).

Table 1. **Retention times of different isomers at 333 K**

product	retention time (min)
2,6-isomer	8.93
1,5-isomer	9.54
2,7-isomer	10.27
1,6-isomer	10.65
1,3-isomer	13.22
1-isomer	11.45
2-isomer	12.06
naphthalene	17.75

Table 2. **A weight percentage of different products obtained by HPLC**

product	393 K	433 K
1-isomer	30.5	3.1
2-isomer	38	58.2
2,6-isomer	0.2	1.0
1,5-isomer	5.8	1.9
2,7-isomer	0.3	2.8
1,6-isomer	4.5	9.1
1,3-isomer	3.2	6.0
H_2SO_4	9	9.6
H_2O	6.7	7.0
naphthalene	1.4	0.6
others	0.4	0.7

The injection loop had a 10 μL capacity. The column was operated at constant temperature (331 ± 0.5 K, thermostat Polystat 86602). A UV−vis spectrophotometric detector was used ($\lambda = 280$ nm).

Using a gradient technique involving two solvents, the different isomers of naphthalenedisulphonic acid could be separated. The compositions of the eluents used were as follows: (A) a binary mixture of water (64% vol) and methanol (36% vol), containing tetrabutylammonium bromide (0.4 g/L) (TBAB); (B) pure methanol (HPLC grade) containing 4 g/L TBAB.

The eluent nonlinear gradient starts with pure A and ends with pure B, at a flow rate of 1.5 mL/min (Figure 2). The standards used for column calibration were developed by Ciba-Geigy (Basel, Switzerland).

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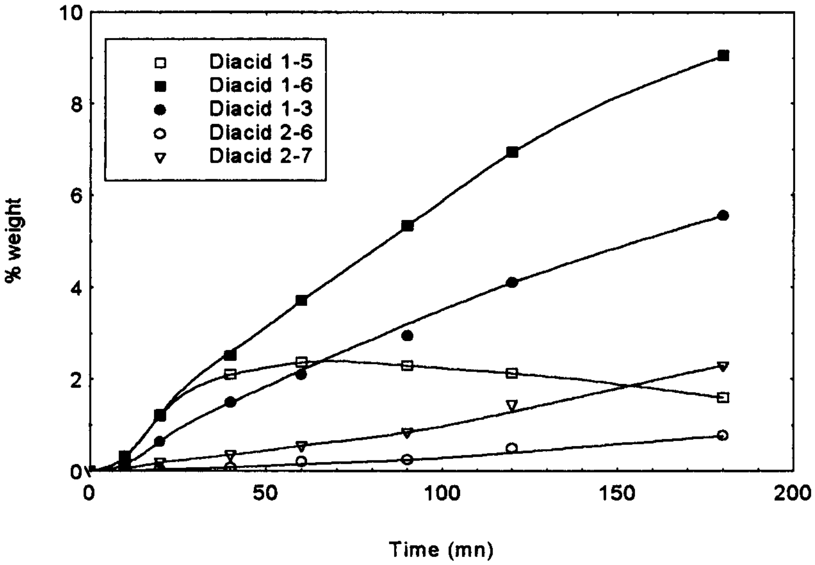

Figure 4. **Diacid concentration versus time at 433 K (weight percent related to initial total mass).**

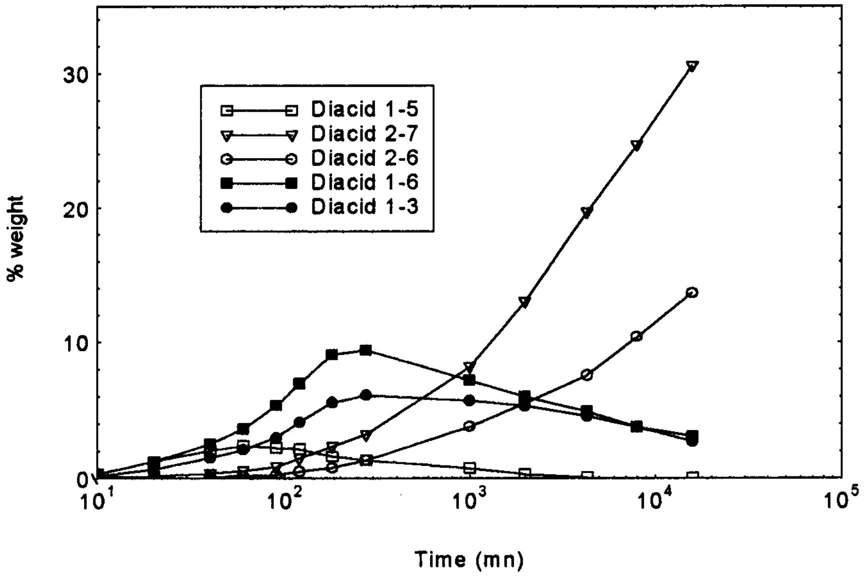

Figure 5. **Diacid concentration versus time at 433 K (weight percent related to initial total mass). The *X* axis is a log scale.**

Under these working conditions, we obtained the retention times presented in Table 1 (the term "retention time" has its generally accepted meaning, that is, the time between injection and detection).

The 1,4-isomer could not be detected in our mixtures. This is in good agreement with the observations of Feirz-David[14] showing that this isomer is not stable enough to be produced directly in the sulphonation mixture.

3. Results and Discussion

Reaction at 393 K. The results are given in Figure 3. Three main conclusions appear immediately:

(1) The reaction leads rapidly to a nearly constant composition of the mixture from the point of view of its diacid content: already before the total amount of oleum has been added (at 60 min, the introduction of oleum going on until 90 mn), about 90% of the final content of all isomers present are in the mixture. After the total introduction of oleum, no significant change in composition appears.

(2) Two classes of products are formed. (a) Three main products are formed: the 1,5-isomer (about 6%), the 1,6-isomer (about 4.5%), and the 1,3-isomer (about 3%). (b) Two minor products are formed: the 2,7-isomer (less than 0.7%) and the 2,6-isomer (less than 0.5%), the latter being formed during the last phase of the reaction, once the oleum content has reached more than 2/3 of its final value. (See Table 2.)

(3) All of these products are formed with poor yields (the best one being near 6%).

Reaction at 433 K. The results are given in Figure 4. The main conclusions of this experiment are as follows.

(1) After the complete introduction of oleum, the reaction still goes on, and even at 180 min, the composition of the reacting mixture varies in time.

(2) Two classes of products can be observed. (a) Products showing a maximum in their concentration curve versus time can be observed (1,5-isomer). These products are kinetically formed but thermodynamically unstable. (b) Products which are thermodynamically stable can be observed. Their concentration constantly increases in time. Two isomers (1,6 and 1,3) show relatively high formation rates (concentration higher than 5% after 3 h). The other ones (2,7 and 2,6) are

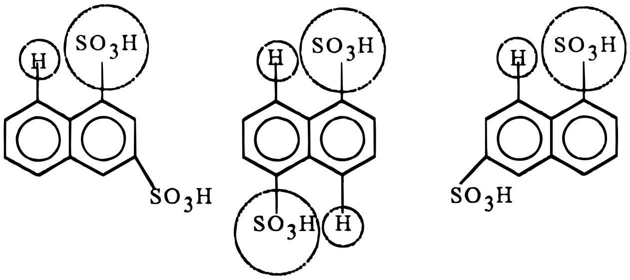

Figure 6. **Steric hindrance for the 1,3-, 1,5-, and 1,6-isomer diacids.**

formed slowly, so that after 3 h, their concentration in the mixture does not exceed 2%. Although long reaction times are not really interesting from the industrial point of view, the sulphonation reaction was allowed to complete over times up to 280 h (Figure 5). The composition was determined after 36 and 260 h. Thus, the final concentration of the 2,6-isomer was 13.6% and the 2,7-isomer concentration was up to 30.5%. These isomers (2,6 and 2,7) are thermodynamically more stable products compared with the higher degree of "peri" strain of the 1,3-, 1,6-, and especially the 1,5-isomers (Figure 6). In fact, there is some steric hindrance which induces isomerization of a sulpho group "peri" to hydrogen, so the concentration of these isomers decreases over time. This shows that these isomers can be prepared with acceptable yields as long as short reaction times are not absolutely required.

4. Conclusion

The improved HPLC technique allowed a good simultaneous determination of all diacids present in the sulphonating mixture. The determinations were reproducibly accurate and fast to carry out.

Increasing temperature lowers the formation of the 1,5-isomer. This effect can be correlated with the presence of two "peri"-positioned sulfo groups in this molecule. The high instability resulting leads to further isomerization when heating continues for a long time: this isomerization results thus in a significant decrease of the 1,5-isomer content with heating time.

Although these effects are present in diacids such as the 1,6- and 1,3-isomers, they are weaker, since just one substituent is in a "peri" position. The most observable effect is their concentration decrease over time at higher temperatures.

The most stable compounds formed either directly or by isomerization of the previous products are the 2,6- and 2,7-diacids. Their concentration increases both by higher sulphonation temperature and by heating of the sulphonating mixture after the initial sulphonation has been completed.

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