MECHANISM OF NITRATION OF PHENOLSULPHONIC ACIDS

K. LEŚNIAK and T. URBANSKI

Institute of Organic Chemistry, Polish Academy of Sciences, Warszawa, Poland

Abstract—Isomeric phenolsulphonic acids and phenol-2,4-disulphonic acid were nitrated with 63% nitric acid. Chromato-polarographic method was used for separation and identification of the products. As known, nitro groups can be introduced: (1) directly into the benzene ring, (2) by substitution for sulphonic groups. It was found that both processes can proceed independently and that the existing views on the mechanism of nitration of sulphonic derivatives of the phenol require correction.

INTRODUCTION

It is well known that in the preparation of picric acid and 2,4-dinitrophenol from phenol by successive treatment with sulphuric and nitric acid, the sulphonic groups protect the phenol from the oxidizing action of the nitric acid. However, the mechanism of this reaction is not exactly known. Usually, investigators were interested in studying this reaction with the intention of increasing the yield of picric acid.

Marqueyrol, Carré and Loriette\(^1\) have found that the yield of picric acid increases when the mixture of phenolsulphonic acids contains a large amount of phenol-2,4-disulphonic acid. King\(^2\) has confirmed that good yield is dependent not only upon the quantity of phenol-2,4-disulphonic acid but also upon the proportion of \(p\)-phenolsulphonic acid. Olsen and Goldstein\(^3\) have suggested that this reaction involves in the first stage the introduction of nitro groups into the aromatic ring.

In order to follow the mechanism of the nitration of phenolsulphonic acids, we examined the action of 63% nitric acid in varying ratios at room temperature and at 95° on separately \(o\)- and \(p\)-phenolsulphonic acids and phenol-2,4-disulphonic acid.

Treatment of phenolsulphonic acids with nitric acid afforded mixtures of

\(^3\) F. Olsen and J. C. Goldstein, Ind. Eng. Chem. 16, 66 (1924).
different nitro-sulphonic derivatives of phenol. The chromato-polarographic method of Kemula\textsuperscript{4} was used to separate and to identify the products. A detailed description of the method was given in another paper.\textsuperscript{5}

**EXPERIMENTAL**

Starting compounds

(a) \textit{o-Phenolsulphonic acid} was prepared according to the method described by Obermiller.\textsuperscript{6} The barium salt was purified by repeated crystallization from water. The free acid was obtained by the action of sulphuric acid in a stoichiometric quantity. (Found: C, 29·6; H, 2·1; Ba, 28·2. Calcd. for $\text{C}_{12}\text{H}_{10}\text{O}_{8}\text{S}_{2}\text{Ba}$: C, 29·8; H, 2·0; Ba, 28·4%).

(b) \textit{p-Phenolsulphonic acid}. The barium salt was obtained by sulphonation of phenol by the method of Rodionov.\textsuperscript{7} Excess of sulphuric acid was neutralised with PbCO$_3$, then with BaCO$_3$. The acid was liberated from the barium salt by treatment with a stoichiometric quantity of sulphuric acid. (Found: C, 29·5; H, 2·2; Ba, 28·2. Calcd. for $\text{C}_{12}\text{H}_{10}\text{O}_{8}\text{S}_{2}\text{Ba}$: C, 29·8; H, 2·0; Ba, 28·4%).

(c) \textit{Phenol-2,4-disulphonic acid}. This acid was obtained according to the method reported by Obermiller.\textsuperscript{6} The barium salt was separated after the density of the solution fell below 1·22 g/ml. Further operations were the same as above.

The influence of the proportion of nitric acid on the course of nitration

Aqueous \textit{p-phenolsulphonic acid} (8·7 g or 0·05 mole/100 ml water) was nitrated with 63% nitric acid in the 1:2, 1:1, and 1:0·5 \textit{p-phenolsulphonic acid} to nitric acid mole ratios at room temperature. The mixture was stirred for several hours and then allowed to evaporate at the same temperature. The resulting crystals or the residue were analysed by the chromato-polarographic method (Fig. 1).

Nitration of phenolsulphonic acids with 63% nitric acid at room temperature

Nitric acid was used in the 1:4 ratio. Samples of the reaction mixture were taken at intervals and introduced onto the chromatographic column. The series of diagrams obtained show the progress of the process in time (Figs. 2–4).


\textsuperscript{5} W. Kemula, K. Leśniak and D. Sybilska, \textit{This Supplement}, p. 53.


\textsuperscript{7} V. M. Rodionov, B. M. Bogoslavski and A. M. Fiedorov, \textit{Laboratornoe rukovodstvo po khimii promezhutochnykh produktov i krasitelei}. Goskhimizdat, Moskva–Leningrad, 1948.
Nitration of phenolsulphonic acids with 63% nitric acid at temperature of 95°

Since the process was very slow at room temperature, we repeated the experiment at a higher temperature. The temperature of 95° was chosen as the average of temperatures used in the manufacture of 2,4-dinitrophenol and picric acid, 90° and 112–115°, respectively. Nitric acid was used in the 1:4 ratio. Phenolsulphonic acids or phenol-2,4-disulphonic acid were placed in test tubes and kept in a thermostat at 95°. At time intervals samples were taken, alkalized with excess sodium hydrogen carbonate and diluted with water. Samples of the solution, 0.1 ml, were analyzed by the chromato-polarographic method, current sensitivity \( S = \frac{1}{1000} \). The chromatograms obtained are given on Figs. 5–7.

RESULTS AND DISCUSSION

Influence of the proportion of nitric acid

The analysis of mixtures obtained as a result of nitration of \( p \)-phenolsulphonic acid with nitric acid used in the 1:0.5; 1:1; 1:2 mole ratios is shown in Fig. 1.

![Fig. 1. Chromato-polarograms of nitration products of \( p \)-phenolsulphonic acid at room temperature and at varying proportions of nitric acid.](image1)

![Fig. 2. Chromato-polarograms of nitration products of \( p \)-phenolsulphonic acid at room temperature.](image2)
Two acids, 2-nitrophenol-4-sulphonic and 2,6-dinitrophenol-4-sulphonic, were detected, the former in each case. The resulting 2,4-dinitrophenol increased in amount as the concentration of nitric acid was raised.

**Reaction at room temperature**

The analysis of mixtures obtained by nitration of p-phenolsulphonic, o-phenolsulphonic and phenol-2,4-disulphonic acids with nitric acid used in the 1:4 mole ratio are given in Figs. 2, 3 and 4.
Mechanism of nitration of phenolsulphonic acids

**p-Phenolsulphonic acid.** Both 2-nitrophenol-4-sulphonic and 2,4-dinitrophenol-4-sulphonic acids were detected. 2,4-Dinitrophenol appeared on the sixth day of nitration.

**o-Phenolsulphonic acid.** Three peaks of nitrophenol-2-sulphonic acids were detected but not identified. They correspond presumably to 4-nitrophenol-2-sulphonic acid, 6-nitrophenol-2-sulphonic acid and 4,6-dinitrophenol-2-sulphonic acid. o-Nitrophenol was found after 18 hr of nitration, 2,4-dinitrophenol after 6 days and picric acid after 71 days.

**Phenol-2,4-disulphonic acid.** Only one peak, probably of 6-nitrophenol-2,4-disulphonic acid, was detected. o-Nitrophenol and picric acid were found after 8 days.

Comparison of Figs. 2, 3 and 4 shows that the first step of nitration is the introduction of nitro group or groups into the free positions of each phenolsulphonic acid. All possible nitrophenolsulphonic acids were formed. In the case of p-phenolsulphonic acid (Fig. 2, after 20 hr) and phenol-2,4-disulphonic acid (Fig. 4, after 5 days) only such products were detected.

The second step, formation of nitrophenols, can proceed:

(a) by replacement of a sulphonic group by a nitro group, e.g. 2,4-dinitrophenol is formed from 2-nitrophenol-4-sulphonic acid (Fig. 2);

(b) by hydrolysis of a sulphonic group to yield a nitrophenol-sulphonic acid, e.g. o-nitrophenol is obtained from 6-nitrophenol-2,4-disulphonic acid (Fig. 4);

(c) by nitration of nitrophenols.

**Reaction at 95°**

The analyses of mixtures obtained by nitration of p-phenolsulphonic, o-phenolsulphonic and phenol-2,4-disulphonic acids with nitric acid used in the 1:4 mole ratio are given in Figs. 5, 6 and 7.

**p-Phenolsulphonic acid** (Fig. 5). 2-Nitrophenol-4-sulphonic acid was present throughout the reaction. 2,6-Dinitrophenol-4-sulphonic acid appeared at the beginning of the reaction (after 5 min.). 2,4-Dinitrophenol (after 5 min.) and picric acid (after 2 hr) were also detected.

After 12 hr of reaction the quantity of picric acid increased, and that of 2-nitrophenol-4-sulphonic acid and 2,4-dinitrophenol decreased.

Disappearance of 2,6-dinitrophenol-4-sulphonic acid after 2 hr of nitration and formation of picric acid at the same time suggests that one of the ways of formation of picric acid is the replacement of the sulphonic group in 2,4-dinitrophenol-4-sulphonic acid by the nitro group. The second possibility is the nitration of 2,4-dinitrophenol. This is corroborated by the fact that the quantity of picric acid increased steadily and that of 2,4-dinitrophenol decreased at the end of reaction.
o-Phenolsulphonic acid (Fig. 6). After 10 min of nitration only one peak and after 2 hr two peaks of nitrophenolsulphonic acids were found. The first peak diminished strongly as the reaction proceeded. After 10 min of the reaction, four nitrophenols were detected, viz., o-nitrophenol, 2,4- and 2,6-dinitrophenols, and picric acid. The quantity of 2,6-dinitrophenol increased moderately and that of 2,4-dinitrophenol rapidly during the course of nitration.

The nitration reaction of o-phenolsulphonic acid can be complicated by rearrangement of o-phenolsulphonic acid into p-phenolsulphonic acid. This isomerisation reaction takes place at 60°. The presence of the two phenolsulphonic acids could lead to four nitrophenolsulphonic acids and made identification of the peaks impossible. On the other hand the rearrangement was not complete, because we found o-nitrophenol and 2,6-dinitrophenol, which were not detected
in the nitration of $p$-phenolsulphonic acid. Thus, these two nitrophenols are characteristic intermediates in the nitration of $o$-phenolsulphonic acid.

It should be pointed out that samples of the reaction liquor at $95^\circ$ of $p$- and $o$-phenolsulphonic acids and nitric acid developed intense colours on alkalization. During the first 30 min of the reaction blood-red colour of increasing intensity develops. After that time the intensity gradually diminishes and changes eventually through orange to yellow.

We are inclined to explain it by admitting the formation of coloured intermediate quinoid addition products (A) and (B) which should pass to nitrophenols:

\begin{align*}
\text{(A)} & \quad \begin{array}{c}
\text{HO} \\
\text{OH} \\
\text{HO} \\
\text{S} \\
\text{NO}_2
\end{array} \\
& \rightarrow \\
\begin{array}{c}
\text{OH} \\
\text{NO}_2
\end{array} + \text{H}_2\text{SO}_4
\end{align*}

\begin{align*}
\text{(B)} & \quad \\
& \begin{array}{c}
\text{HO} \\
\text{OH} \\
\text{SO}_3\text{H} \\
\text{NO}_2
\end{array} \\
& \rightarrow \\
\begin{array}{c}
\text{OH} \\
\text{NO}_2
\end{array} + \text{H}_2\text{SO}_4
\end{align*}

We suggest this scheme as a tentative explanation of the substitution of sulphonic group in phenolsulphonic acids by the nitro group.

*Phenol-2,4-disulphonic acid* (Fig. 7). After 10 min of nitration only one peak, presumably that of 6-nitrophenol-2,4-disulphonic acid, was obtained. After 1 hr, a second peak of nitrophenolsulphonic acid appeared and 2 hr later disappeared. Three nitrophenols were detected: $o$-nitrophenol, 2,4-dinitrophenol, and picric acid.

The appearance of a second nitrophenolsulphonic acid during the nitration process suggested that the replacement of a sulphonic group in 6-nitrophenol-2,4-disulphonic acid by a nitro group took place. A hydrolytic process leading to a nitrophenol-mono-sulphonic acid is also possible. The hydrolysis of one of the sulphonic groups to phenol-2,4-disulphonic acid followed by nitration resulted in nitrophenolsulphonic acids too. Thus, the identification of the second peak was impossible.

Comparison of Figs. 5, 6 and 7 shows that, during the nitration at $95^\circ$, the first step of reaction was the introduction of nitro group or groups into the free positions of the ring of the phenolsulphonic acids. The fact that not all possible nitrosulphonic acids were detected is presumably caused by the high reaction rate of further reactions of these acids. Beside nitration, hydrolysis or rearrangement of sulphonic groups in phenolsulphonic acids are possible.
Fig. 7. Chromato-polarograms of nitration products of phenol-2,4-disulphonic acid at 95°.
The second step reactions, replacement and hydrolysis of sulphonic groups in nitrosulphonic acids and nitration of nitrophenols, proceeded very quickly—the nitrophenols and picric acid were detected after 5 and 10 min. of the nitration. The nitrophenolsulphonic acids content decreased and that of nitrophenols, especially picric acid, increased as the nitration proceeded.