Acid and Basic Hydrolyses of *p*-Nitrophenyl Benzenesulfonate*

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In previous papers we have reported on studies of both the acid¹⁾ and alkaline²⁾ hydrolyses of phenyl benzenesulfonate, and have suggested that these reactions proceed through the S_N2-type process, in which a nucleophilic attack of either water or the hydroxide ion takes place on the sulfur atom. It was also shown that there was no oxygen exchange in the ester during the hydrolyses, unlike the cases of the esters of carboxylic acid.³⁾ There was an incorporation of only one equivalent amount of ^{18}O in the benzenesulfonic acid isolated from reaction products. In the case of the acid hydrolysis, however, it was found that the phenol isolated from the hydrolysis of the ester with ^{18}O-enriched water was incorporated with the excess ^{18}O.

Although the reaction proceeded via the acyl-oxygen cleavage, the phenol formed was found to exchange gradually its oxygen with that of the medium water during the acid hydrolysis.

During the course of our study of the oxygen exchange between phenols and water in both acid and alkaline media, *p*-nitrophenol was found to undergo the oxygen exchange more readily than the other substituted phenols studied.⁴⁾ Since the substitution of the nitro group on the benzene ring of an

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* Paper IV of Reactions of Phenols and Phenolic Esters.

1) S. Oae, T. Fukumoto and R. Kiritani, This Bulletin, **36**, 346 (1963).

2) D. R. Christman and S. Oae, *Chem. & Ind.*, **1959**, 1251.

3) M. L. Bender, *J. Am. Chem. Soc.*, **73**, 1626 (1951).

4) S. Oae and R. Kiritani, This Bulletin, **37**, 770 (1964).

aromatic compound usually causes a strong activation of the ortho- and para-positions of the benzene ring, and hence makes a nucleophilic attack at these positions easier, it is not surprising to expect an aryl-oxygen cleavage, especially in the alkaline hydrolysis of the titled compound. Therefore, one may expect that the substitution of a nitro group at the para-position, namely in the titled compound, will change the course of the hydrolyses.

Recently, Bunnett and Bassett, Jr.[5] have shown through their kinetic study that a number of mono- and dinitro phenol esters of *p*-toluenesulfonic acid are found to undergo both sulfur-oxygen and carbon-oxygen scissions in the reactions with a few such strong nucleophilic reagents as thiophenolate ions, piperidine and methoxide ions.

Meanwhile, Vizgert et al.[6] have also found that the nitro group at either ortho- or para-positions of the phenolic portion of substituted phenyl benzenesulfonates showed a marked accelerating effect in the alkaline hydrolysis of substituted phenyl benzenesulfonates.

The present research was designed to investigate further the mechanisms of both acid and alkaline hydrolyses of the titled compound by means of both the ^{18}O tracer technique and a kinetic study of the hydrolyses.

Results and Discussion

Acid Hydrolysis. — The acid hydrolysis of the titled compound was very sluggish and was found to take place only above 160°C in a sealed tube using 10 N hydrochloric acid, much as in the case of phenyl benzenesulfonate. The ester and 10 N hydrochloric acid, made by dissolving hydrogen chloride gas into ^{18}O-enriched water, were sealed in a tube; the tube was then heated at 180°C for 6 hr. The reaction was stopped before completion in order to see if the hydrolysis reaction proceeds through a reversible addition intermediate; thereby unhydrolyzed ester was recovered, together with the hydrolysis products, i. e., *p*-nitrophenol and benzenesulfonic acid.

Meanwhile, the same reactants were also heated in sealed tubes at 180°C for 24 hr., the ester was completely hydrolyzed, and the products were isolated. In order to see the effects of acid concentration on the hydrolysis, the hydrolysis was also carried out using 3.5 N hydrochloric acid prepared with ^{18}O-enriched water. When the mixtures of the ester and the 3.5 N hydrochloric acid were also heated at 180°C for 6 hr., 12 hr., and 24 hr. in sealed tubes, it was found that the hydrolysis was half completed after the mixtures had been heated for 24 hr. The reaction products obtained in nearly quantitative yields after the complete hydrolysis were purified in the following ways: *p*-nitrophenol was sublimed, while benzenesulfonic acid was treated with *S*-benzylthiuronium chloride to give the *S*-benzylthiuronium sulfonate. The recovered ester was recrystallized from ethanol, and all these samples were subjected to ^{18}O analysis by the usual method.[7] The results are shown in Table I.

In all cases, the ^{18}O content of the recovered ester was found to be 0.20 atom% ^{18}O. As this value represents the natural ^{18}O atom%, it illustrates that there is no exchange of ^{18}O in the ester during this reaction process, as in the case of phenyl benzenesulfonate. This observation clearly excludes any reversible prior addition of water molecules or hydronium ions during the hydrolysis of the titled compound and suggests that the overall reaction is irreversible. The observation also seems to suggest that the reaction is a S_N2-type synchronous one-step process initiated by the attack of water oxygen on the sulfur atom, which bears a formal double-positive charge as in the case of the hydrolysis of phenyl benzenesulfonate. Two alternative mechanistic

TABLE I. DISTRIBUTION OF THE ^{18}O LABEL IN ACID HYDROLYSIS PRODUCTS

Run	Reaction time, hr.	^{18}O Atom% of aq. HCl soln.	^{18}O Atom% of products		
			p-Nitrophenol	Benzenesulfonic acid	Recovered ester
1	6	1.58 (3.5 N)	—	—	0.20
2	12	1.58 (3.5 N)	0.20 (0.26)*	—	0.20
3	24	1.58 (3.5 N)	0.23 (0.29)	0.62	0.20
4	6	1.58 (10 N)	0.22 (0.26)	0.63	0.20
5	24	1.58 (10 N)	0.37 (0.91)	0.65	—

* Numerical values in parentheses represent the ^{18}O concentration of phenolic oxygen calculated from the concentration of whole molecule by neglecting the ^{18}O exchange nitro group.

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[5] J. F. Bunnett and J. Y. Bassett, Jr., *J. Am. Chem. Soc.*, **81**, 2104 (1959).

[6] a) R. V. Vizgert, *Zhur. Obshchei Khim.*, **28**, 1873 (1958); b) R. V. Vizgert and E. K. Savchuk, ibid., **28**, 2114 (1958); c) R. V. Vizgert, E. K. Savchuk and O. A. Purib, ibid., **31**, 194 (1961).

[7] S. Oae, T. Kitao and Y. Kitaoka, *J. Am. Chem. Soc.*, **84**, 3359 (1962).

schemes are also conceivable for this reaction; one involves the nucleophilic attack of water on the aromatic ring carbon para to the nitro group, and the other is a S_N1-type process involving a slow cleavage of a sulfur-oxygen or carbon-oxygen bond, followed by rapid solvolysis, to form sulfonic acid and *p*-nitrophenol. However, the aromatic S_N2-type mechanism cannot be accepted, since the benzenesulfonic acid isolated was found to be incorporated with one atom equivalent amount of ^{18}O of ^{18}O-enriched water (0.66 atom%); this cannot be reconciled with the aromatic S_N2-type mechanism involving the carbon-oxygen cleavage.

The S_N1-type mechanism involving the cleavage of the carbon-oxygen linkage is not plausible. The S_N1 process of this type did not take place in the acid hydrolysis of phenyl benzenesulfonate. The substitution of a strong electron-withdrawing group, such as a nitro group, at the para-position will suppress even more the S_N1-type C–O bond cleavage. On the other hand, the S_N1-type cleavage of a S–O bond is also very difficult, since it will leave an additional positive charge on the sulfur atom, which already bears double formal positive charges, and the cleavage would require an enormous energy.

The remaining and the most probable pathway is the S_N2-type process initiated by the attack of the water molecule on the sulfur atom. If the reaction proceeds through this process, the benzenesulfonic acid will be incorporated with one equivalent amount of ^{18}O and the *p*-nitrophenol will remain natural. While benzenesulfonic acid was incorporated with ^{18}O just as much as is required from this process, *p*-nitrophenol was always incorporated with an excess of ^{18}O above the natural concentration, and the amount of ^{18}O incorporation appeared to increase with prolonged heating, as is shown by Table I.

In separate experiments we have carried out the oxygen exchange reactions of *p*-nitrophenol, phenol, benzenesulfonic acid and nitrobenzene in the same acidic (10 N) solutions. The results are shown in Table II.

TABLE II. OXYGEN EXCHANGE REACTION OF SOME COMPOUNDS IN THE ACIDIC SOLUTION

Compound	Reaction time, hr.	^{18}O Atom % of aq. HCl soln.	^{18}O Atom % of products
p-Nitrophenol	6	1.58	0.40 (0.80)*
	24	1.58	0.37 (0.72)
Nitrobenzene	24	1.58	0.20
Phenol	5	0.8	0.37
	24	0.77	0.73
Benzenesulfonic acid	5	0.8	0.23
	24	0.8	0.24

* See footnote in Table I.

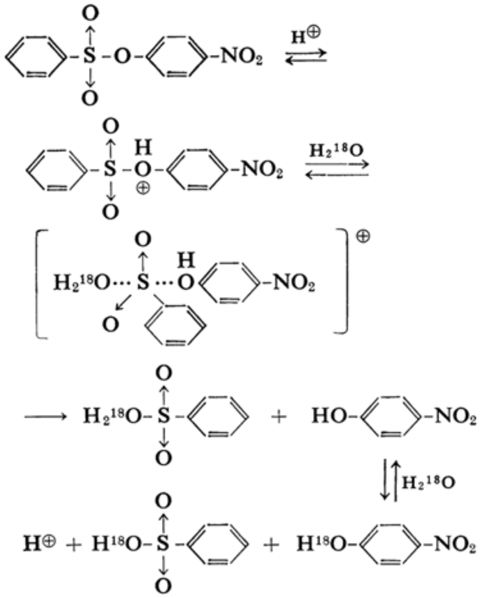


Fig. 1

There was no apparent oxygen exchange in the nitro group; however, *p*-nitrophenol was found to undergo a more facile oxygen exchange than phenol in 6 hours of treatment. This observation also indicates that the *p*-nitrophenol formed during the acid hydrolysis of the ester gradually changed its phenolic oxygen atom with a solvent of ^{18}O-enriched water. Thus, the overall reaction scheme of this acid-catalyzed hydrolysis of the ester is considered to be the S_N2 process, in which the water molecule attacks the sulfur atom, shown by Fig. 1, giving benzenesulfonic acid and *p*-nitrophenol, which then undergoes further phenolic oxygen exchange with the solvent water.

Alkaline Hydrolysis.—The titled ester was dissolved in ^{18}O-enriched water containing 1% potassium hydroxide, and the solution was refluxed for 8 hr. Since the reaction was partially completed, some recovered esters were obtained, together with the reaction products, benzenesulfonic acid and *p*-nitrophenol. Similarly, the ester was hydrolyzed with ^{18}O-enriched water containing 10% potassium hydroxide and refluxed for 8 hr. In this way the reaction was completed, and benzenesulfonic acid and *p*-nitrophenol were obtained in nearly quantitative yields. All the products and the recovered ester thus obtained were subjected to the usual ^{18}O analysis; the results are shown in Table III.

Here again, the ^{18}O content of the recovered ester was not increased more than the natural ^{18}O content during this partial hydrolysis

TABLE III. DISTRIBUTION OF THE ^{18}O LABEL IN ALKALINE HYDROLYSIS PRODUCTS

Run	Reaction time, hr.	^{18}O Atom% of aq. KOH soln.	^{18}O Atom% of products		
			p-Nitrophenol	Benzenesulfonic acid	Recovered ester
1	8	1.58 (1%)	0.26 (0.38)*	0.54	0.20
2	8	1.55 (10%)	0.48 (1.04)	0.57	—

* See footnote in Table I.

TABLE IV. OXYGEN EXCHANGE REACTION OF SOME COMPOUNDS IN THE ALKALINE SOLUTION

Compound	Reaction time, hr.	^{18}O Atom% of aq. KOH soln.	^{18}O Atom% of products
p-Nitrophenol	8	1.58 (1% KOH)	0.21 (0.23)*
	8	1.55 (10% KOH)	0.58 (1.34)
Nitrobenzene	8	1.55 (10% KOH)	0.20
Benzenesulfonic acid	8	1.55 (10% KOH)	0.22
	8	1.58 (1% KOH)	0.21

* See footnote in Table I.

process. The overall reaction was irreversible, and obviously there was no reversible prior addition of hydroxyl ions to the sulfur atom. However, there were a few significant differences between the acid and alkaline hydrolysis of this compound. While the benzenesulfonic acid obtained in the acid hydrolysis was always incorporated with one equivalent amount of the ^{18}O (0.66 atom%) resulting from the ^{18}O-enriched water used, the alkaline hydrolysis yielded benzenesulfonic acid, whose ^{18}O incorporation was somewhat lower (0.54, 0.57 atom%) than that of the ^{18}O-enriched water used. *p*-Nitrophenol was also incorporated with ^{18}O; its ^{18}O incorporation was apparently larger when the potassium hydroxide solution used was more concentrated.

In separate experiments the oxygen exchange reactions were carried out in aqueous potassium hydroxide under the same conditions in order to test the oxygen exchange of these products with solvent water. The results are shown in Table IV.

It is interesting to note that the ^{18}O exchange was negligible when the concentration of potassium hydroxide was small (1%), but that it became substantial when the alkaline concentration was increased to 10%. On the other hand, the hydrolysis in the 1% potassium hydroxide solution gave *p*-nitrophenol noticeably enriched with ^{18}O and benzenesulfonic acid, the ^{18}O concentration of which was apparently lower than what was to be expected from a straight-forward S_N2 process involving the nucleophilic attack of the hydroxyl ion on the sulfur atom, as is shown in Fig. 2.

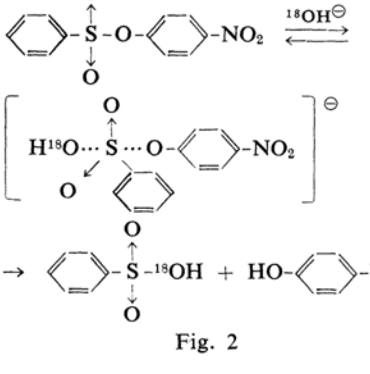


Fig. 2

The small increase in the ^{18}O in the *p*-nitrophenol and the decrease in ^{18}O in the sulfonic acid can be accounted for if one assumes that a portion of the reaction proceeded via an aromatic S_N2 process involving the C–O bond cleavage, as is shown in Fig. 3.

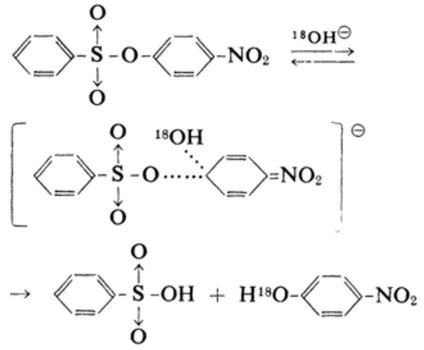


Fig. 3

Therefore, at least in the alkaline hydrolysis with a 1% potassium hydroxide solution, the two reactions appears to compete, though the S_N2 process involving the nucleophilic attack on the sulfur atom is by far the predominant path (about 78—80%). In the concentrated alkaline solution (10% potassium hydroxide), the oxygen-exchange was found to take place substantially for *p*-nitrophenol. This somewhat obscures the mechanistic diagnosis with the ^{18}O data of the hydrolysis products. One can see, however, that the concentration of

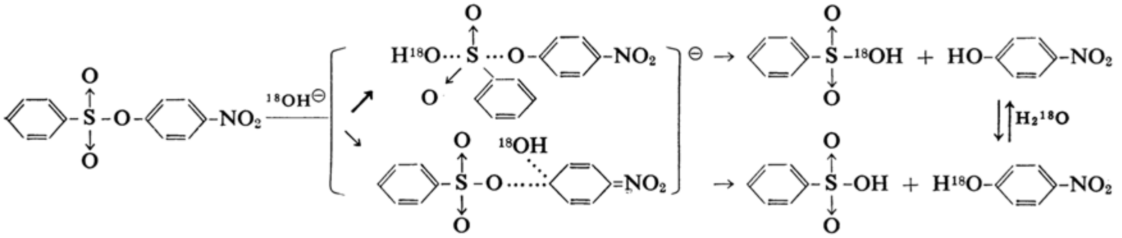
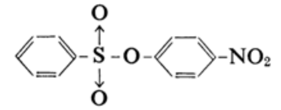


Fig. 4

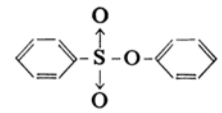
^{18}O in the nitrophenol after 8 hr. of ^{18}O exchange was markedly higher (0.58) than that in the same compound obtained in the hydrolysis (0.48). Moreover, the ^{18}O concentration of the *p*-nitrophenol obtained by the hydrolysis was far smaller than that of the water used. From these results, it is clear that the major portion of the reaction proceeded via the usual S_N2 process involving a nucleophilic attack on the sulfur atom (Fig. 2), much as in the earlier findings with other strong nucleophiles.[5] In contrast to the marked increase in ^{18}O in the nitrophenol in the hydrolysis in a 10% alkaline solution, no reduction of ^{18}O concentration in benzenesulfonic acid resulted from the change of alkalinity from 1% to 10%. Instead, there was only a slight increase, if any. This may mean that in the concentrated alkaline solution a small portion of the reaction also proceeds via an aromatic S_N2 process involving C-O bond cleavage and that the resulting nitrophenol undergoes subsequent ^{18}O exchange. Thus, the overall reaction scheme can be represented by the two competing process shown by Figs. 2 and 3; however, the ordinary S_N2 process involving the attack of the hydroxyl ion on the sulfur atom is the predominant path. A schematic illustration is shown in Fig. 4.

The rates of the alkaline hydrolyses of two esters, *p*-nitrophenyl benzenesulfonate, and phenyl benzenesulfonate, have been investigated at 49.5±0.05°C in alkaline aqueous 50% dioxane. An inspection of the data reveals that the rate of the former is substantially higher than that of the latter, as Russian workers have shown previously.[7]

$k_2=78.6\times10^{-3}$ sec^{-1} mol./l. for



$k_2=0.416\times10^{-3}$ sec^{-1} mol./l. for



This means that the substitution of a nitro group at a para-position markedly facilitates the nucleophilic attack of the hydroxide ion on phenyl benzenesulfonate. At first it was thought that the rate-acceleration due to the *p*-nitro group is related to the facile nucleophilic attack of the hydroxide ion on the aromatic carbon atom via an aromatic S_N2 process; however, the ^{18}O data do not support this idea. The presence of a *p*-nitro group apparently reduces the electron density around not only the aromatic C_1 atom, but also the sulfonyl sulfur atom, thereby causing a large acceleration of the nucleophilic attack of the hydroxide ion on both positions.

Experimental

***p*-Nitrophenyl Benzenesulfonate.**—*p*-Nitrophenol (28 g., 0.2 mol.) was dissolved in 160 ml. of pyridine. The mixture was cooled in ice water, and an equimolar amount of benzenesulfonyl chloride (35 g.) was stirred into it drop by drop and then allowed to stand at 0°C overnight. The reaction mixture was then poured in ice water. After filtering, the precipitate was repeatedly washed with water and aqueous sodium bicarbonate to remove the pyridinium hydrogen chloride completely and then recrystallized from ethanol. Ninety grams of a colorless plate, *p*-nitrophenyl benzenesulfonate, were obtained (89% purified yield); m. p. 88—89°C.

Hydrolysis in an Acidic Solution.—*p*-Nitrophenyl benzenesulfonate (1 g.) was dissolved in 5 ml. of 10 N hydrochloric acid containing 1.58 atom % of ^{18}O. The mixture was kept for 24 hr. at 180°C in a sealed tube. Then the sealed tube was broken, and all the contents were extracted with ether. The aqueous layer was then evaporated down to 2 ml. To this solution a few drops of hyrochloric acid and *S*-benzylthiuronium chloride (0.7 g.) were added, and 1.3 g. of *S*-benzylthiuronium salt of benzenesulfonic acid (white plate) was obtained, m. p. 148.5°C. This corresponds to 0.55 g. of benzenesulfonic acid (97% yield). The ether extract was dissolved in aqueous sodium carbonate and extracted with ether to remove the unhydrolyzed ester (though none of the ester was extracted). The alkaline layer was then neutralized with weak hydrochloric acid and extracted with ether again. From the combined ether extract, the ether was removed and the residual mass was sublimated twice to obtain 0.46 g. of pure *p*-nitrophenol, m. p. 113°C (92.4% yield).

Partial Hydrolysis in an Acidic Solution.—The same reaction mixture used for the complete acid hydrolysis was made and then heated in a sealed tube for 6 hr. at 180°C. When the products were treated as described above, the unhydrolyzed ester (0.8 g.) and *p*-nitrophenol (0.08 g.) were obtained from the ether layer, while benzenesulfonic acid (0.1 g.) was isolated from the aqueous layer as the *S*-benzylthiuronium sulfonate. Some more experiments on the partial hydrolyses were carried out using the ester and 3.5 N hydrochloric acid containing 1.58 atom% ^{18}O at 180°C for 6 hr., 12 hr. and 24 hr. The products were also treated as has been described above.

Hydrolysis in an Alkaline Solution. — When potassium hydroxide (1.9 g., 0.034 mol.) was dissolved in 15 ml. of water containing 1.58 atom% ^{18}O, the ^{18}O content of this solution was found to decrease to 1.55 atom% ^{18}O. The ester (1.2 g., 0.0042 mol.) was dissolved in this solution (10%) and refluxed for 8 hr. The products were extracted with ether (though none of the unhydrolyzed ester was obtained from the ether layer). The alkaline layer was treated as described above, and 0.5 g. of *p*-nitrophenol and 0.6 g. of benzenesulfonic acid were isolated.

Partial Hydrolysis in an Alkaline Solution.—The ester (1.2 g.) was dissolved in the solution of 30 ml. of water-^{18}O and 0.38 g. (0.0068 mol.) of potassium hydroxide; this solution, containing 1.58 atom% ^{18}O, was then refluxed for 8 hr. The recovered ester and the reaction products, *p*-nitrophenol and benzenesulfonic acid, were obtained as has been described above. The ester (1.2 g.) was dissolved in a solution of 60 ml. of 50% dioxane-water-^{18}O containing 0.38 g. of potassium hydroxide, and the solution was kept 50°C for 1 hr. After evaporation, the residue was treated as has been described above. The results were the same as those obtained in a heterogeneous system of aqueous solutions.

The Kinetic Determination of the Alkaline Hydrolyses of *p*-Nitrophenyl Benzenesulfonate and Phenyl Benzenesulfonate. — Solutions of *p*-nitrophenyl benzenesulfonate (3.5529 g., 0.0127 mol.) in 100 ml. dioxane and 100 ml. of aqueous potassium hydroxide (0.0382 mol./100 ml.) were separately immersed in a water thermostat set at 49.5±0.05°C for at least 30 min. before mixing. The hydrolyses were then started by mixing the two solutions by means of vigorous shaking. The rates were followed by pippetting out an aliquot portion of the mixture from time to time, then quenching it with an excess of standard hydrochloric acid, and finally back-titrating with standard potassium hydroxide using a pH-meter (the endpoint was PH 4.5).

In a separated experiment, a solution of phenyl benzenesulfonate (2.9769 g., 0.0127 mol.) in 100 ml. dioxane was hydrolyzed in the way which has been described above.

In both hydrolyses, the initial concentrations of the two components, the ester and the hydroxide ion, were made in a 1 : 3 mol. ratio; therefore, one mole equivalent of the hydroxide ion should be left in the solution at the end of the reaction, because every one mole of ester is considered to consume two moles of hydroxide ions in the reaction.

Therefore, the rates were calculated following the second-order rate kinetic equation shown below.

$$kt=\frac{1}{b-2a}\ln\frac{a(b-2x)}{b(a-x)}$$

a: Initial hydroxide ion concentration
b: Initial ester ion concentration
x: Concentration reacted
t: Time

A plot of $\ln\frac{a(b-2x)}{b(a-x)}$ versus t gave straight lines in both cases, as is shown by Fig. 5.

Isotopic Analysis.—The ^{18}O analysis was performed as in a previous experiment.[7]

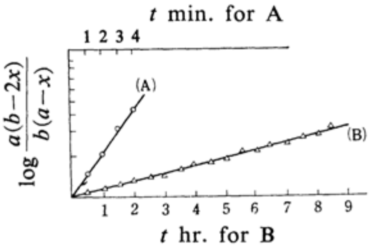


Fig. 5

(A) *p*-Nitrophenyl benzenesulfonate
(B) Phenyl benzenesulfonate

Summary

The mechanisms of both the acid- and the alkaline-catalyzed hydrolyses of *p*-nitrophenyl benzenesulfonate have been investigated by means of the ^{18}O-tracer technique. The acid-catalyzed hydrolysis apparently proceeds via a S_N2-type process involving the nucleophilic attack of water on the sulfur atom, with a S–O bond cleavage. Much as with the earlier findings concerning other nucleophiles, the major portion of the alkaline hydrolysis was also found to proceed through a S_N2 process which involves the nucleophilic attack of the hydroxide ion on the sulfur atom, with a S–O bond fission; only a small portion of the reaction appeared to proceed via an aromatic S_N2-type process.

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