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CARBONYL PARTICIPATION DURING THE HYDROLYSIS OF ARYL BENZENESULPHONATES

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ABSTRACT: Rate enhancement to the extent of about 10^6 for the hydrolysis of aryl benzenesulphonates due to participation by the neighbouring carbonyl group is reported.

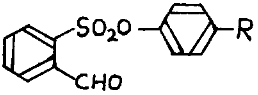
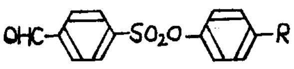
As a part of an extended programme of the study of neighbouring group effects, we have studied the rates of basic hydrolysis of a series of phenyl esters of benzenesulphonic acids and the solvolysis of the corresponding sulphonyl chlorides both having formyl group in 2- and 4-positions with respect to the sulphonyl group.

In Table I are summarised the rates of basic hydrolysis of 2- and 4-formylbenzenesulphonates of para substituted phenols. The Hammett 'ρ' for 2-formyl-derivatives 1-5 is 0.1 and that for 4-formyl derivatives 6-10 is 1.59. Use of sodium carbonate for the hydrolysis of 1-5 was necessary as the rates with sodium hydroxide was too fast to be followed by titrimetry. In order to obtain the rate enhancement, the rate constants for the hydrolysis of 5 and 10 were determined using sodium hydroxide under comparable conditions viz., at 25.6°C in aq. acetone. The hydrolysis of 10 could be followed conveniently by titrimetry ($k=17.3 \times 10^{-4} LM^{-1}S^{-1}$) but that of 5 could be followed only with a stopped-flow spectrophotometer ($k=7072\ LM^{-1}S^{-1}$) obtained by following the appearance of 4-nitrophenoxide at 400 nm). The ratio of the rate constants for 5 and 10 is about 4×10^6. These results clearly show that the 2-formyl group brings about a dramatic increase in the rate and a decrease in the 'ρ' value for the hydrolysis of sulphonate esters. Clearly the hydrolysis of the two series of compounds viz., 1-5 and 6-10 involve different mechanisms.

Although carbonyl group participation as a means of rate enhancement has been well recognised,[1,2] certain features of this phenomenon had not been fully explored. The present study clearly establishes the role of the leaving group. The neglegible 'ρ' value in the case of 2-formyl derivatives indicates that the cleavage of the leaving group is fast compared to the attack of the nucleophile on the carbonyl group. In a previous paper[3] we had shown that a similar situation exists in the carbonyl assisted hydrolysis of carboxylic acid esters.

In table 2 are summarized the rates of solvolysis of 2- and 4-formyl benzenesulphonyl chlorides. It is clear that they solvolyze with similar rates. The 'm' value[4] for 2-formylbenzenesulphonyl chloride is 0.3 and that for 4-formylbenzenesulphonyl chloride is 0.21. These results indicate a S_N2 type of reaction in both the cases and non-operation of carbonyl assisted solvolysis.

Table 1: Rate constants[a] for the basic hydrolysis of 2- and 4-formylbenzene sulphonates[5] in 50 % aq. dioxane.

Entry		$k_2^b \times 10^4$ $LM^{-1}s^{-1}$	Entry		$k_2^c \times 10^4$ $LM^{-1}s^{-1}$
1	R = OMe	46.5	6	R = OMe	5.05
2	Me	47.6	7	Me	5.64
3	H	49.4	8	H	8.50
4	Br	52.0	9	Br	23.87
5	NO_2	66.4	10	NO_2	185.3

a) Determined by titrimetric procedure b) at 5°C using sodium carbonate ρ =0.1
c) at 46.5°C using sodium hydroxide. ρ = 1.59

Table 2: Rate constants[a] for the solvolysis of 2- and 4-formylbenzenesulphonyl chlorides at 30°C in aq. acetone.

Percentage acetone V/V	70	60	50	40
$2\text{-}OHC\text{-}C_6H_4\text{-}SO_2Cl$ $k_1 \times 10^4 s^{-1}$	8.75	12.6	23.3	34.3
$4\text{-}OHC\text{-}C_6H_4\text{-}SO_2Cl$ $k_1 \times 10^4 s^{-1}$	7.2	10.7	13.0	17.3

a) Determined under pseudo first order conditions by conductometry.

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5) All the compounds used in the present study were characterized by physical constants, spectroscopic and analytical data. Detailed experimental procedures can be obtained from the authors on request.

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