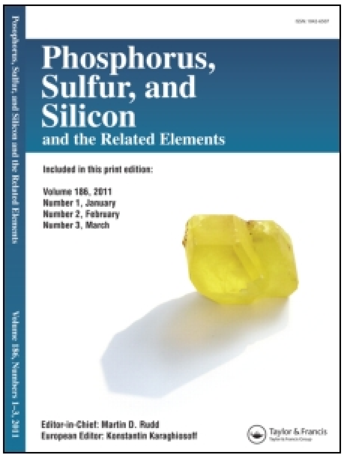

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SULFONATION AND SULFATION IN THE REACTION OF 4-METHYLPHENOL WITH CONCENTRATED SULFURIC ACID

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SHORT COMMUNICATION SULFONATION AND SULFATION IN THE REACTION OF 4-METHYLPHENOL WITH CONCENTRATED SULFURIC ACID

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The sulfonation of 4-methylphenol (**1**) in concentrated sulfuric acid ranging in concentration from 81.6–112.2% H_2SO_4 has been studied. In ≤98.5% H_2SO_4 the initial product is exclusively the 2-sulfonic acid (**1**-2-S) and the eventual one **1**-2,6-S_2. In fuming sulfuric acid, the additional products are the cyclic sulfate sulfonate anhydride **2**, **2**-5-S, **2**-6-S and **2**-3,5-S_2. The precursor of **2**-5-S is **2** and that of **2**-6-S **1**-2,6-S_2. In 112.2% H_2SO_4 **2**-5-S yields slowly **2**-3,5-S_2 [(cf. Scheme 1)

INTRODUCTION

The sulfonation of phenols can successfully be effected with SO_3 in aprotic solvents[2,3] and with concentrated sulfuric acid which then serves both as reagent and solvent.[4,5] With SO_3 as reagent the initial product is the phenyl hydrogen sulfate which is slowly converted into the phenolsulfonic acid via O-desulfonation and subsequent C-sulfonation if the phenol is in excess, but via initial C-sulfonation and subsequent O-desulfonation if the phenol is deficient relative to the SO_3.[2] With sulfuric acid ranging in concentration from 74–90% H_2SO_4 the sulfonic acids are formed directly from the (unprotonated) phenol as the reactive substrate species. In fact, in that range of sulfuric acid concentration potassium phenyl sulfate is rapidly hydrolyzed before being sulfonated.[4]

Recently we observed in the sulfonation of 4-methoxyphenol that the 2- to 3-sulfonic acid ratio increases strongly upon increasing the sulfuric acid concentration from 68 to 98% H_2SO_4.[6] A priori the variation in the sulfonation isomer ratio may be explained in terms of a gradual change-over in both the substrate entity undergoing sulfonation (from the phenol to its hydrogen sulfate) and the reactive sulfonating entity (from $H_3SO_4^+$ to $H_2S_2O_7$[4]). With the aim of obtaining further information as to this problem we have studied the sulfuric acid sulfonation of 4-methylphenol.

RESULTS AND DISCUSSION

4-Methylphenol (**1**) has been reacted in a very large excess of concentrated sulfuric acid varying in concentration from 81.6 to 112.2% H_2SO_4 (i.e. fuming sulfuric acid containing 54.2% "free" SO_3) mainly at 20°C in order to study the effect of any initial sulfation on the sulfonation. The product composition of the

TABLE I

Sulfonation of 4-methylphenol (1) in concentrated sulfuric acid

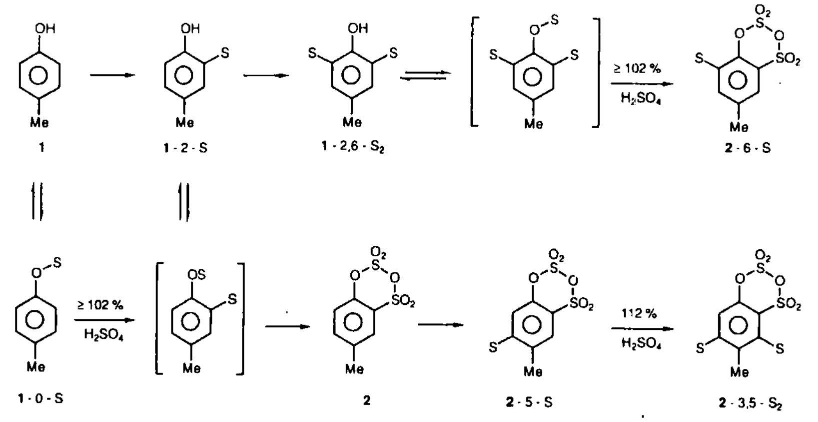
H_2SO_4 wt-%	Temp °C	Reaction time, ks	Product composition,%[a,b]						
			1-O-S	**1**-2-S	**2**[c]	**1**-2,6-S_2	**2**-5-S	**2**-6-S	**2**-3,5-S_2
81.6	30	84.2		100					
84.9	30	86.4		93		7			
90.0	30	1.5		93		7			
98.5	20	1.8		68		32			
		6.8		9		91			
		1100		—		100			
101.9	20	2.7			32	53	2	13	
		14.8			21	44	13	22	
		72.7			14	42	22	22	
106.0	20	2.2			44		5	51	
		86.4			10		39	51	
		510			—		49	51	
112.2	20	0.3	15		35		3	47	
		1.5	—		37		16	47	
		82.0			16		25	48	11

[a] S stands for SO_3H.

[b] In all the experiments the substrate conversion was complete.

[c] For the structure of **2** see Scheme 1.

various reaction mixtures for various reaction times are compiled in Table I. In sulfuric acid ≤ 98.5% H_2SO_4 the initial sulfonation product is 4-methylphenol-2-sulfonic acid (**1**-2-S) and the eventual one (**1**-2,6-S_2). The conversion into **1**-2,6-S_2 is of the first order with respect to **1**-2-S and the sulfonation rate coefficient of **1**-2-S at 35°C is 6 times higher with 98.5 than 90.0% H_2SO_4. In fuming sulfuric acid the initially observed products are **1**-2,6-S_2, the methylbenzo[e]-1,3,2,4-dioxadithiin 2,2,4,4-tetraoxide **2** [i.e. the cyclic 1,2-(sulfate sulfonate) anhydride of **1**-2,O-S_2], and its sulfonic acids **2**-5-S, **2**-6-S and **2**-3,5-S_2. For the experiments in 101.9 and 106.0% H_2SO_4 it appears that the sum of amounts of **1**-2,6-S_2 and **2**-6-S is independent of the reaction time and so is the sum of **2** and **2**-5-S. Apparently **1**-2,6-S_2 yields exclusively **2**-6-S and **2** exclusively **2**-5-S, as shown in Scheme 1. After 2 days of reaction **2**-6-S started to precipitate from the 106.0%



SCHEME 1

H_2SO_4 solution. The identity of this product was proven by isolation of the precipitate after 7 days of reaction at 20°C and recording the ^1H NMR spectrum after dissolving it in ^2H_2O. The spectrum appeared to be identical with that of **1**-2,6-S_2 which is the hydrolyzed product of **2**-6-S. In 112.2% H_2SO_4 **2**-5-S is slowly sulfonated to yield **2**-3,5-S_2.

In conclusion it appears that in the sulfuric acid sulfonation of 4-methylphenol no substitution *ortho* to the methyl substituent occurs in the initial sulfonation. Only in the subsequent ring sulfonations, *viz.* in that of the sulfate sulfonate anhydride **2** and in **2**-5-S does sulfonation *ortho* to the methyl group take place. The first observation infers that the variation of the 2- to 3-sulfonic acid ratio observed for the sulfonation of 4-methoxyphenol with concentrated aqueous sulfuric acid has to be ascribed to the gradual change-over in the sulfonating entity from $H_3SO_4^+$ to $H_2S_2O_7$, as is discussed more extensively in the paper.[6]

EXPERIMENTAL

4-Methylphenol was obtained from Janssen Chimica and used as such. The reaction procedures and the methods of assignment of the products and of the determination of the composition of the reaction mixtures were as described before.[6] The ^1H NMR spectra were recorded using a Jeol-60 spectrometer. The relevant ^1H NMR data of the reaction products are given in Table II.

TABLE II

^1H NMR data of the sulfo products of 4-methylphenol in sulfuric acid as solvent

4-Methylphenol substituents[a]	H_2SO_4 wt-%	δ(ppm)				
		2-H	3-H	4-Me	5-H	6-H
O-S	112.2	7.30(d)[b]	7.00(d)[b]	2.40(s)		
2-S	98.5		7.25(s)	2.28(s)	7.15(d)[b]	6.75(d)[b]
1-OSO_2OO_2S-2	101.9–112.2		7.60(s)	2.60(s)	—7.27(br.s)—	
2,6-S_2	98.5–101.9		7.65(s)	2.38(s)		
	0[d]		7.70(s)	2.35(s)		
1-OSO_2OO_2S-2;5-S	101.9–112.2		7.78(s)	2.68(s)		7.88(s)
1-OSO_2OO_2S-2;6-S	101.9–112.2		7.85(d)[c]	2.52(s)	7.70(d)[c]	
1-OSO_2OO_2S-2;3,5-S_2	112.2			2.93(s)		8.08(s)

[a] S stands for SO_3H.

[b,c] $J \approx 8$ and ≈ 3 Hz respectively.

[d] ^2H_2O solution, pH < 7.

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