

## SULPHONATION OF POLYMETHYLBENZENSULPHONIC ACIDS

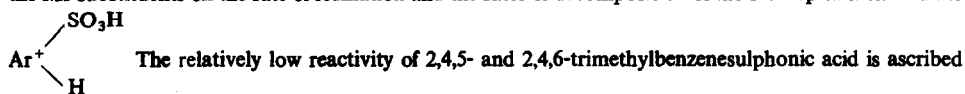
### EVIDENCE FOR A BUTTRESSING EFFECT\*†

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**Abstract**—The rate of sulphonation of a series of polymethylbenzene sulphonic acids in 99.6% H<sub>2</sub>SO<sub>4</sub> has been determined at 25.0°. The observed rate order for the various substrates (2,3,4-Me<sub>3</sub> > 2,4-Me<sub>2</sub> > 2,3-Me<sub>2</sub> > 2,4,5-Me<sub>3</sub> = 2,4,6-Me<sub>3</sub> > 2-Me > 4-Me) is explained in terms of steric and electronic effects of the Me substituents on the rate of formation and the rates of decomposition of the  $\sigma$ -complex intermediate



to a very low rate of conversion of the  $\sigma$ -complex into the sulphonic acid product due to buttressing of the Me group *ortho* to the reaction centre at position 2 by the sulphonic acid substituent at position 1.

For the sulphonation of benzenesulphonic acid and *p*-xylene-sulphonic acid in 104.4% H<sub>2</sub>SO<sub>4</sub> at 25° the ratio of *para*- to *meta*- and of 6- to 5-substitution are 0.030 and 0.078 respectively; the corresponding activation parameter differences are  $\Delta H_p^\ddagger - \Delta H_m^\ddagger = 2.2 \pm 0.2$  kcal/mole,  $\Delta H_6^\ddagger - \Delta H_5^\ddagger = 2.4 \pm 0.1$  kcal/mole,  $\Delta S_p^\ddagger - \Delta S_m^\ddagger = 1.3 \pm 0.7$  eu and  $\Delta S_6^\ddagger - \Delta S_5^\ddagger = 3.0 \pm 0.4$  eu. The entropy difference data illustrate that the steric requirements are smaller for sulphonation *ortho* to an isolated Me group than to a Me group which is flanked by an *ortho*-sulphonic acid group.

AS PART of our programme on aromatic sulphonation we now report the relative rates of sulphonation of several mono- and polymethylbenzenesulphonic acids. This study was made in connection with studies on the sulphonation of toluene and the xylenes. The results for toluene<sup>2-5</sup> and the xylenes<sup>6</sup> have been reported previously.

The rates of a series of methylbenzenesulphonic acids were determined in 99.6% H<sub>2</sub>SO<sub>4</sub> at 25°, all sulphuric acid samples originating from one stock solution. The experimental pseudo first-order rate constants  $k_{1,exp}$  are listed in Table 1.

With *o*-toluenesulphonic acid two positions are available for substitution, *viz* the 4- and 6-position. The NMR spectrum obtained on sulphonation of 5 wt-% *o*-toluenesulphonic acid with 104.4% H<sub>2</sub>SO<sub>4</sub> shows the same aromatic hydrogen ABX pattern as the spectrum obtained on starting with *p*-toluenesulphonic acid. These spectra are further identical with the spectrum obtained on starting with toluene, a spectrum which was reported recently.<sup>8</sup> Thus *o*-toluenesulphonic acid is sulphonated

\* Aromatic sulphonation part 27. Preceding paper: *Rec. Trav. Chim.* **88**, 1298 (1969).

† Part of this work has been described in the Thesis of A. J. Prinsen.

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TABLE 1. RATES OF SULPHONATION IN 99.6 ± 0.1% H<sub>2</sub>SO<sub>4</sub> AT 25.0°

Methyl substituted benzenesulphonic acid (substrate)	Disulphonic acid product	${}_{\text{exp}}k_1 \cdot 10^5, \text{sec}^{-1}$
2-Me-	4-Me-1,3-benzenedisulphonic acid	0.40 <sup>a</sup>
4-Me-	4-Me-1,3-benzenedisulphonic acid	0.024 <sup>a</sup>
2,3-Me <sub>2</sub> -	4,5-Me <sub>2</sub> -1,3-benzenedisulphonic acid	5.9
2,4-Me <sub>2</sub> -	4,6-Me <sub>2</sub> -1,3-benzenedisulphonic acid	41
3,4-Me <sub>2</sub> -	4,5-Me <sub>2</sub> -1,3-benzenedisulphonic acid	0.69
2,3,4-Me <sub>3</sub> -	4,5,6-Me <sub>3</sub> -1,3-benzenedisulphonic acid	68
2,4,5-Me <sub>3</sub> -	2,4,5-Me <sub>3</sub> -1,3-benzenedisulphonic acid	1.1
2,4,6-Me <sub>3</sub> -	2,4,6-Me <sub>3</sub> -1,3-benzenedisulphonic acid	1.1

<sup>a</sup> Data obtained by graphical intrapolation from ref 7.

mainly at the 4-position. The upper limit of substitution at the 6-position was estimated from the absence of the corresponding Me hydrogen peak from the spectrum of the sulphonation mixtures to be at most 0.5%.\*

This observation is in accordance with a prediction based on a comparison of the rates of sulphonation of *o*- and *p*-toluenesulphonic acid,<sup>10</sup> but conflicts with a recent report that toluene-2,6-disulphonic acid can be obtained by sulphonation of *o*-toluenesulphonic acid.<sup>11</sup>

TABLE 2. TEMPERATURE DEPENDENCE OF RATES OF SULPHONATION

Arenesulphonic acid	Temp. °C	${}_{\text{exp}}k_1 \cdot 10^5, \text{sec}^{-1}$	
		98.7% H <sub>2</sub> SO <sub>4</sub>	99.5% H <sub>2</sub> SO <sub>4</sub>
<i>o</i> -Toluene-(A)	25.0		0.33
	65.0		13.9
	85.0		141
<i>p</i> -Toluene-(B)	25.0		0.018
	65.0		0.56
	85.0		7.0
<i>m</i> -Xylene-4-(C)	25.0	3.1	16
	45.0	25.2	192
	55.0		398
	60.0	105	
	75.0	341	
Mesitylene-(D)	45.0	1.65	
	60.0	9.7	
	75.0	42.3	

In 99.5% H <sub>2</sub> SO <sub>4</sub> : $\Delta H_A^* - \Delta H_B^* = 0.6 \pm 1.5 \text{ kcal/mole}$
$\Delta S_A^* - \Delta S_B^* = 9 \pm 4 \text{ eu}$
In 98.7% H <sub>2</sub> SO <sub>4</sub> : $\Delta H_C^* - \Delta H_D^* = -4.7 \pm 0.7 \text{ kcal/mole}$
$\Delta S_C^* - \Delta S_D^* = -8 \pm 2 \text{ eu}$

\* The Me hydrogen NMR absorption of a Me substituted benzene is shifted 0.25 ppm downfield on introduction of one sulphonic acid group *ortho* to the Me group; on introduction of two sulphonic acid groups in *ortho*-position, the downfield shift of the Me hydrogen absorption is about 0.6 ppm.<sup>9</sup>

With *m*-xylene-4-sulphonic acid in 104.4% H<sub>2</sub>SO<sub>4</sub> the main sulphonation product was shown to be *m*-xylene-4,6-disulphonic acid by direct NMR analysis of the reaction mixture; the content of *m*-xylene-2,4-disulphonic acid was estimated to be <0.5%\* from the absence of the corresponding Me hydrogen NMR absorption peaks.

The temperature dependence of the rate of sulphonation of some arenesulphonic acids is shown in Table 2, together with the difference in activation parameters for sulphonation of *o*- and *p*-toluenesulphonic acid on the one hand, and of *m*-xylene-4-sulphonic acid and mesitylenesulphonic acid on the other.

The isomer distribution in the sulphonation of benzene-sulphonic acid and of *p*-xylenesulphonic acid has been determined in fuming sulphuric acid (Table 3). Both the isomer distributions are independent of the oleum composition. For both substrates the activation parameter differences for substitution of one position *para* and *meta* to the sulphonic acid substituent have been calculated (Table 3).

TABLE 3. SULPHONATION OF ARENESULPHONIC ACIDS IN FUMING SULPHURIC ACID

Substrate	%H <sub>2</sub> SO <sub>4</sub>	Temp °C	Isomer distribution, %		$\Delta H_p^* - \Delta H_m^*$ kcal/mole	$\Delta S_p^* - \Delta S_m^*$ eu			
			<i>para</i> (±0.5) <sup>a</sup>	<i>meta</i> (±0.5) <sup>a</sup>					
Benzenesulphonic acid	101.2	25.0	3.4	96.6	2.2 ± 0.2	1.3 ± 0.7			
	104.4	25.0	2.4	97.6					
		66.0	3.3	96.7					
		100.0	4.4	95.6					
		129	5.3	94.7					
		160	7.6	92.4					
		106.9	25.0	2.4			97.6		
		109.0	25.0	2.9			97.1		
	<i>p</i> -Xylenesulphonic acid	101.2	25.0	7.4			92.6	2.4 ± 0.1	3.0 ± 0.4
		104.4	0.0	5.0			92.8		
		25.0	7.2	92.8					
		50.5	8.9	91.1					
		77.0	12.7	87.3					
		100.5	14.7	85.3					
		106.9	25.0	7.1	92.9				
		109.0	25.0	6.4	93.6				

\* With *p*-xylenesulphonic acid *para* and *meta* refers to the formation of *p*-xylene-2,6- and *p*-xylene-2,5-disulphonic acid respectively.

Prior to a discussion on the rate data, the protonation of arenesulphonic acid substrates has to be considered. Information on the relative degree of protonation of some of the methylbenzenesulphonic acids was obtained according to a method proposed.<sup>12</sup> This method is based on an assumed linear correlation between the  $pK_{BH^+}$  value of the conjugate acid of an -SO<sub>2</sub>-group containing compound (*in casu* a sulphone, HSO<sub>4</sub><sup>-</sup>, H<sub>2</sub>SO<sub>4</sub> and an arenesulphonic acid) and its S-O stretching frequency, defined as  $\nu_{SO} = \frac{1}{2}(\nu_{sym} + \nu_{asym})$ .<sup>13</sup> The results are given in Table 4. In 99.6% H<sub>2</sub>SO<sub>4</sub>, the acid concentration employed for the determination of the rates of the various substrates, the fraction of arenesulphonic acid which was calculated to be present in its protonated form is negligibly small. This conclusion is in accordance

\* See previous page.

TABLE 4.  $pK_{BH^+}$  AND  $|BH^+|/|B|$  VALUES FOR SOME ARENESULPHONIC ACIDS, CALCULATED FROM THEIR S—O STRETCHING FREQUENCIES

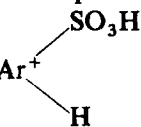
Sulphonic acid	$\nu_{sym}$	$\nu_{asym}$	$\nu_{SO}^a$	$pK_{BH^+}$	$ BH^+ / B $	
	cm <sup>-1</sup>				99.5% H <sub>2</sub> SO <sub>4</sub>	104.4% H <sub>2</sub> SO <sub>4</sub>
C <sub>6</sub> H <sub>5</sub> SO <sub>3</sub> H	1188	1362	1275	-14.6	0.0003	0.11
2-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> H	1189	1357	1273	-14.6	0.0003	0.11
4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> H	1170	1354	1262	-14.1	0.0011	0.34
2,4-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> SO <sub>3</sub> H	1178	1342	1260	-14.0	0.0013	0.43

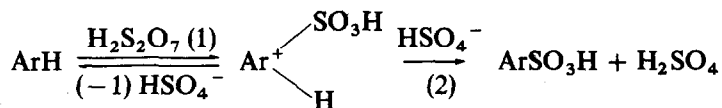
<sup>a</sup> The absorption frequencies were obtained with a Perkin-Elmer IR spectrometer, model 125, from solutions of the anhydric sulphonic acids.

with independent direct evidence from cryoscopic and conductivity measurements to the effect that *p*-toluenesulphonic acid behaves as a non-electrolyte in 100% H<sub>2</sub>SO<sub>4</sub>.<sup>7</sup>

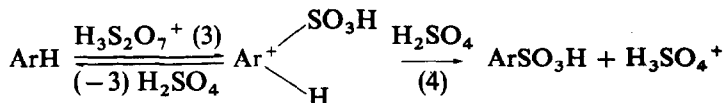
In 104.4% H<sub>2</sub>SO<sub>4</sub>, the acid concentration employed for the isomer distribution studies, a substantial fraction of the sulphonic acid will be present in the unreactive protonated form.

#### DISCUSSION

It has been suggested<sup>14</sup> that the sulphonation of aromatic compounds in sulphuric acid of a composition close to 100% H<sub>2</sub>SO<sub>4</sub> proceeds via Ar<sup>+</sup>  as  $\sigma$ -complex intermediate. At the aqueous side of 100% H<sub>2</sub>SO<sub>4</sub> the reaction proceeds mainly by the sequence



in which the rates of the steps (-1) and (2) are of the same order of magnitude. At the fuming side of 100% H<sub>2</sub>SO<sub>4</sub> up to about 104% H<sub>2</sub>SO<sub>4</sub> the sulphonation proceeds by the sequence



with reaction (3) as rate limiting step.

The present rate and isomer distribution data will be discussed in terms of substituent effects—including steric effects—on the rate of formation and the rates of decomposition of the common  $\sigma$ -complex intermediate.

At 25° in 99.6% H<sub>2</sub>SO<sub>4</sub> the rate of sulphonation of *o*-toluenesulphonic acid is 17 times that of the *para*-isomer. This difference in rate is mainly due to a  $9 \pm 4$  eu smaller entropy of activation for sulphonation *ortho* than for sulphonation *para* to a Me group,

the enthalpy of activation being about equal. The difference in entropy of activation for step (1) for substitution *para* and *ortho* to a Me group, as determined in the sulphonation of toluene,<sup>5</sup> is  $4.9 \pm 0.4$  eu, i.e. equal to the present difference within the experimental error.

The higher reactivity of *m*-xylene-4-sulphonic acid relative to the toluenesulphonic acids for sulphonation in 99.6% H<sub>2</sub>SO<sub>4</sub> is thought to originate in step (1). It may be explained in terms of an increase in stabilization of the transition state of step (1), as result of additional hyperconjugative electron release to the reaction centre by the extra Me group.

Introduction of a second Me group *ortho* to the position to be sulphonated leads to a sharp decrease in rate. Thus the rates of sulphonation of both 2,4,5- and 2,4,6-trimethylbenzenesulphonic acid in 99.6% H<sub>2</sub>SO<sub>4</sub> are appreciably smaller than the rate of *m*-xylene-4-sulphonic acid (Table 1), while the rate of sulphonation at the 2-position in *m*-xylene-4-sulphonic acid in 104.4% H<sub>2</sub>SO<sub>4</sub> is at least 200 times less than that at the 6-position.

The enthalpy and the entropy of activation are greater for the sulphonation of mesitylenesulphonic acid than for that of *m*-xylene-4-sulphonic acid. The activation parameter differences are both opposite in sign to that expected if the difference in rate between the two substrates were mainly determined by step (1). The rate order for the sulphonation of the toluenesulphonic acids and *m*-xylene-4-sulphonic acid has been explained in terms of reaction (1). Accordingly it is proposed that the effect of the proton removing step (2) on the over-all rate of sulphonation is different for mesitylenesulphonic acid and *m*-xylene-4-sulphonic acid.

The relative rate constants for the sulphonation of one of the equivalent positions of substitution in *m*-xylene-4-, 2,3,4-trimethylbenzene- and 2,4,6-trimethylbenzenesulphonic acid in 99.6% H<sub>2</sub>SO<sub>4</sub> at 25° are 1.00, 1.66 and 0.013 respectively (Table 1). The relative rate constants for sulphonation of one of the equivalent positions of the corresponding hydrocarbons *m*-xylene, 1,2,3- and 1,3,5-trimethylbenzene in 81.5% H<sub>2</sub>SO<sub>4</sub> at 12.3° are 1.00, 1.4 and 2.2 respectively.<sup>15</sup> A comparison of these two sets of rate data again indicates that the sulphonation of mesitylenesulphonic acid is strongly retarded.

The lower reactivity of mesitylenesulphonic acid, as compared with *m*-xylene-4-sulphonic acid, is the result of its higher enthalpy of activation. The increase in the overall  $\Delta H^*$  is thought to arise from an increase in the activation enthalpy of reaction (2), as result of a form of buttressing:<sup>16, 17</sup> the sulphonic acid group at position 1 of mesitylenesulphonic acid (2,4,6-trimethylbenzene-1-sulphonic acid) buttresses the Me group at position 2, thus rendering the bending away of this Me group in the plane of the aromatic ring during the reaction step (2) extremely difficult.\* Rate retardation due to this type of buttressing is also to be expected on sulphonating the 3-position of 2,4,5-trimethylbenzenesulphonic acid and the 2-position of *m*-xylene-4-sulphonic acid. This is in fact observed as will now be discussed. The rate of sulphonation of 2,4,5-trimethylbenzenesulphonic acid is relatively low, as is evident from a comparison of the rates of sulphonation of *o*-xylene-3-, *o*-xylene-4-, 2,3,4-trimethylbenzene- and 2,4,5-trimethylbenzenesulphonic acid. For introduction of a methyl group *ortho* to

\* The internal strain problem of the present disulphonic acids with four vicinal substituents has some analogy with that of the homomorphs of 2,6-dimethyl-1-butylbenzene for which compounds an internal strain of 17 kcal/mole was estimated.<sup>18, 19</sup>

the reaction centre leads to an increase in rate by a factor of 12 on going from *o*-xylene-3-to 2,3,4-trimethylbenzenesulphonic acid, whereas it leads to an increase by a factor of only 1.6 on going from *o*-xylene-4- to 2,4,5-trimethylbenzenesulphonic acid (Table 1).

Overcrowding as result of four adjacent substituents will also be encountered on sulphonating *m*-xylene-4-sulphonic acid at the 2-position. In the absence of an overcrowding effect the ratio of substitution at the 2- and 6-position in first approximation will be equal to the partial rate factor ratio  $^{Me}f_0 : ^{Me}f_p$ . This ratio, as determined from the rate ratio of sulphonation in 99.6%  $H_2SO_4$  of the 2-position in *p*-toluenesulphonic acid and the 4-position in *o*-toluenesulphonic acid is 0.03 (Table 1), whereas this ratio as determined from the rate ratio of 2- and 4-substitution in the sulphonation of *m*-xylene and toluene with the sulphonating entity  $H_2S_2O_7$  are  $0.34 \pm 0.01^1$  and  $0.58 \pm 0.01^5$  respectively. In fact, the ratio of substitution at the 2- and 6-position on sulphonation of *m*-xylene-4-sulphonic acid with 104.4%  $H_2SO_4$  at room temperature is very much less than these values, viz  $< 0.005$ , illustrating again rate retardation due to buttressing.

A comparison of the steric requirements for sulphonation *ortho* to an isolated Me group and a Me group which is buttressed by an *ortho*-sulphonic acid group can be obtained using *o*-toluenesulphonic acid and *p*-xylene-2-sulphonic acid as substrates.

The ratio of substitution at the 6- and 4-position of *o*-toluenesulphonic acid in 104.4%  $H_2SO_4$  is only  $< 0.005$ , whereas the  $^{Me}f_0 : ^{Me}f_p$  ratio, as determined from the sulphonation of toluene with the sulphonating entity  $H_2S_2O_7$  is  $0.58 \pm 0.01^5$ .

As to the sulphonation of *p*-xylene-2-sulphonic acid in 104.4%  $H_2SO_4$  the difference in activation entropy for substitution at the 5- and 6-position is  $3.0 \pm 0.4$  eu (Table 3).

This value is greater than the difference of  $1.3 \pm 0.7$  eu for substitution of the 4- and one 3-position of benzenesulphonic acid. These entropy data illustrate that the steric requirements for substitution *ortho* to a Me group are increased by introduction of a

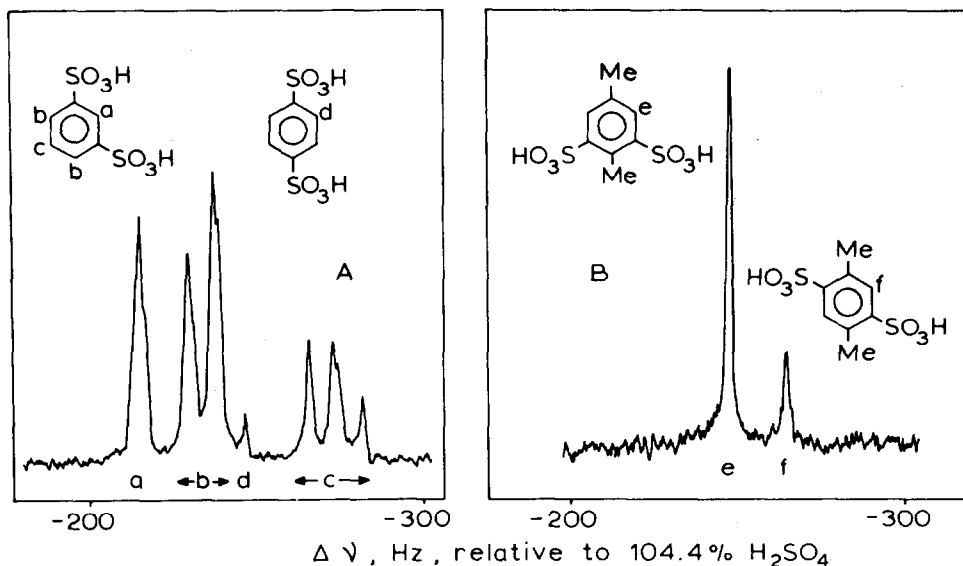


FIG. 1 Aromatic hydrogen patterns of the NMR-spectra of the sulphonation mixtures of benzenesulphonic acid (A) and *p*-xylenesulphonic acid (B) in 104.4%  $H_2SO_4$ .

sulphonic acid group at the other *ortho*-position. This conclusion is in accordance with the interpretation of the relative low reactivities of 2,4,5- and 2,4,6-trimethylbenzenesulphonic acid in sulphonation discussed in the preceding paragraphs. The isomer distribution data of the *p*-xylene disulphonic acid (Table 3) conflict with the very early reports, quoted by Suter,<sup>20</sup> that the main product on sulphonation of *p*-xylene with 50% fuming sulphuric acid or with chlorosulphuric acid at 150° yields mainly the 2,5-disulphonic acid.

#### EXPERIMENTAL

1,3,5-Trimethylbenzenesulphonic acid (Aldrich Chemical Co.) was converted into its potassium salt. Potassium 1,2,3- and potassium 1,2,4-trimethylbenzenesulphonate were prepared via reaction of the corresponding aromatic hydrocarbons with chlorosulphuric acid.<sup>21</sup> The position of the sulphonate groups in the compounds was ascertained by NMR analysis.<sup>1, 9</sup> The preparation of the other sulphonic acids has been described.<sup>3, 22, 23</sup> Anhydric arenesulphonic acids (for the IR measurements) were obtained by distillation of the corresponding hydrated products in a bulb distillation apparatus<sup>24</sup> at ~70°/0.02 mm Hg.

The H<sub>2</sub>O content of the "anhydric" sulphonic acids was determined from NMR spectra of the acids in D<sub>2</sub>O from the ratio of the H<sub>2</sub>O absorption to the Me or aromatic hydrogen absorption. The water content of the anhydric sulphonic acids was found to be <1 wt-%. The rate constants of sulphonation were determined according to standard procedures.<sup>7</sup> The isomer distribution studies with benzenesulphonic acid and *p*-xylenesulphonic acid were made as follows: 50 mg of the sodium arenesulphonate were dissolved in 1.0 ml 104.4% H<sub>2</sub>SO<sub>4</sub> at the appropriate temp. The isomer distribution of the disulphonic acid formed was determined from the aromatic hydrogen absorption pattern of the NMR spectrum of the reaction mixture. Typical NMR spectra are shown in Fig 1.

The content of *para*-isomer of the benzenedisulphonic acids was calculated in two ways. First from the ratio of the area of peak d and the total area of the aromatic hydrogens and secondly from the ratio of the area of (b + c) and the total area of the aromatic hydrogens (Fig 1A). The values listed in Table 4 are the average values of the data calculated by the two methods.

The ratio of *p*-xylene-2,5- relative to *p*-xylene-2,6-disulphonic acid was calculated from the ratio of the peaks e and f (Fig 1B).

The NMR spectra were obtained with a HA 100 Varian NMR spectrometer using 104.4% H<sub>2</sub>SO<sub>4</sub> as the internal standard.

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