Aromatic Sulphonation. Part 65.[1] On the Sulphonation of 1-Methylnaphthalene and Polymethylbenzenes

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The isomer distributions for the mono-, di-, and tri-sulphonation of 1-methylnaphthalene in respectively 90.1, 98.4, and 110% sulphuric acid at 25 °C have been determined. The degree of sulphonation at the 2-position is smaller for sulphonation in 98.4 than 90.1% H_2SO_4. The results are discussed in terms of sulphonation by $H_3SO_4^+$, $H_2S_2O_7$, and $H_2S_4O_{13}$ as sulphonating entities and compared with those of the polymethylbenzenes. The mechanistic conclusion that the sulphonation with $H_3SO_4^+$ has a ' later ' transition state than that with $H_2S_2O_7$ is in agreement with the results of simple Hückel MO calculations. The deviating behaviour for the 2-substitution of 1-methylnaphthalene is ascribed to enhanced steric control, because of the shorter C(1)—C(2) bond distance in 1-methylnaphthalene as compared with toluene. The isomer distribution for the mono-, and di-sulphonates resulting from 1-methylnaphthalene with SO_3 in nitromethane is also reported.

ELECTROPHILIC aromatic substitution has recently attracted renewed interest. Fundamental questions have been raised about the reaction path in nitration [2] and halogenation.[3] The character of the electrophilic entity reactive in sulphonation has been established.[4a,b] Electrophilic aromatic substitution has also been the subject of theoretical treatment.[5] In order to obtain insight into the behaviour of polyaromatic compounds we thought it of interest to study first the sulphonation of methyl substituted naphthalenes. The results on naphthalene itself were published some time ago.[6] Here we describe the results of the sulphonation of 1-methylnaphthalene under various conditions. The results of 2-methylnaphthalene have recently been reported.[7]

Some results are available for other electrophilic substitutions of 1-methylnaphthalene. Protonation,[8] chloromethylation,[9] succinoylation,[10] bromination,[11] and Friedel–Crafts acylation,[12] occur mainly at the 4-position. Chlorination [13] also gives mainly the 4-derivative; a recent study revealed that substantial amounts of addition products are also formed.[2] The order of reactivity of the various positions for protiodetritiation was established as $4 > 2 > 5 > 8 > 7 \simeq 3 > 6$.[14] The substitution rate order for the nitration with HNO_3 in acetic anhydride was found to be $4 > 2 > 8 > 5 > 3$ (>6 and 7), but depends on the reagent employed.[15] The product isolated on mononitration [15,16] contains mainly the 4-nitro derivative, with some of the 2-, 3-, 5-, and 8-isomers. Nitration of 1-methyl-4-nitronaphthalene yields mainly the 4,5-dinitro compound with some of the 2,4-, 4,8-, and an unknown dinitro isomer.[16] Sulphonation of 1-methylnaphthalene at 5—40 °C with concentrated sulphuric acid [17] and chlorosulphonic acid [18] at −7 to 0 °C gives mainly the 4- with some 5-sulphonic acid. At 110 °C the 3-sulphonic acid [19] is formed, whereas with sulphuric acid at 165—185 °C the major product is the 7-sulphonic acid.[20] With SO_3–dioxan the sulphonation proceeds exclusively at the 4-position.[21]

RESULTS

Sulphonation with 90.1% H_2SO_4: *Monosulphonic Acids.*—The sulphonation of 1-methylnaphthalene with 90.1% sulphuric acid at 25 °C leads to the formation of monosulphonic acids. The product composition was followed by ^1H n.m.r. spectroscopy (Figure 1). The isomer distribution for monosulphonation was determined, by extrapolation to zero reaction time, as 27% 1-methylnaphthalene-2-sulphonic acid and 73% 1-methylnaphthalene-4- and -5-sulphonic acids. In the sulphuric acid reaction mixture the 4- and 5-isomer cannot be distinguished by ^1H n.m.r. After isolation of the potassium sulphonates the 5-isomer could be identified in D_2O solution by its n.m.r. signals at δ 8.77 (4-H), 8.32 (6-H), and 2.27 (1-CH_3). The isomer distribution of the 2-, 4-, and 5-sulphonic acids was determined

[1] Part 64, T. A. Kortekaas, H. Cerfontain, and J. M. Gall, *J.C.S. Perkin II*, 1978, 445.
[2] R. B. Moodie and K. Schofield, *Accounts Chem. Res.*, 1976, **9**, 287.
[3] P. B. D. de la Mare, ' Electrophilic Halogenation,' Cambridge University Press, 1976.
[4] (*a*) C. W. F. Kort and H. Cerfontain, *Rec. Trav. chim.*, 1969, **88**, 1298; H. Cerfontain and C. W. F. Kort, *Internat. J. Sulfur Chem.* (*C*), 1971, **6**, 123; (*b*) J. K. Bosscher and H. Cerfontain, *Rec. Trav. chim.*, 1968, **87**, 873; *Tetrahedron*, 1968, **24**, 6543.
[5] A. Streitwieser, jun., ' Molecular Orbital Theory for Organic Chemists,' Wiley, New York, 1961.
[6] H. Cerfontain and A. Telder, *Rec. Trav. chim.*, 1967, **86**, 527.
[7] P. H. Gore and A. S. Siddiquei, *J.C.S. Perkin I*, 1972, 2344.
[8] G. A. Olah, G. D. Mateescu, and Y. K. Mo, *J. Amer. Chem. Soc.*, 1973, **95**, 1865.
[9] P. Cannonne, Le-Knac Huy, and W. Forst, *Canad. J. Chem.*, 1971, **49**, 4073.
[10] A. Connu, J. Ulrich, and K. Persaud, *Chim. Analyt.*, 1965, **47**, 357.
[11] R. D. Topsom and J. Vaughan, *J. Chem. Soc.*, 1957, 2842.
[12] R. D. Haworth and C. R. Marvin, *J. Chem. Soc.*, 1932, 2720.
[13] G. Gum, P. B. D. de la Mare, and M. D. Johnson, *J. Chem. Soc.* (*C*), 1967, 1590.
[14] C. Eaborn, P. Golborn, R. E. Spilett, and R. Taylor, *J. Chem. Soc.* (*B*), 1968, 1112.
[15] P. G. E. Alcorn and P. R. Wells, *Austral. J. Chem.*, 1965, **18**, 1377.
[16] H. W. Thompson, *J. Chem. Soc.*, 1932, 2310.
[17] (*a*) G. T. Morgan and A. E. Coulson, *Chem. and Ind.*, 1934, 73; (*b*) S. H. Morrell, G. B. Pickering, and J. C. Smith, *J. Inst. Petroleum*, 1948, **34**, 677.
[18] (*a*) R. E. Steiger, *Helv. Chim. Acta*, 1930, **13**, 173, 177; (*b*) V. Veselý, F. Šturša, H. Olejníček, and E. Rein, *Coll. Czech. Chem. Comm.*, 1929, **1**, 493.
[19] V. Veselý, and F. Šturša, *Coll. Czech. Chem. Comm.*, 1931, **3**, 328.
[20] K. Dziewoński and T. Waszkowski, *Bull. Internat. Acad. polonaise*, 1929A, 604 (*Chem. Abs.*, 1931, **25**, 1241).
[21] E. Gudrinicce and I. Lielbriedes, *Latvijas Valsts. Univ. Kim. Fak., Zinatniskie Raksti.* 15, 1957, **5**, 291 (*Chem. Abs.*, 1959, **53**, 18,922).

from the ^{1}H n.m.r. spectrum of such a quantitatively worked-up sample to be 25, 60, and 15% respectively.

Sulphonation with 98.4% H_2SO_4: *Disulphonic Acids.*—With 98.4% sulphuric acid the disulphonation of 1-methylnaphthalene at 25 °C is completed in 26 h. The presence of

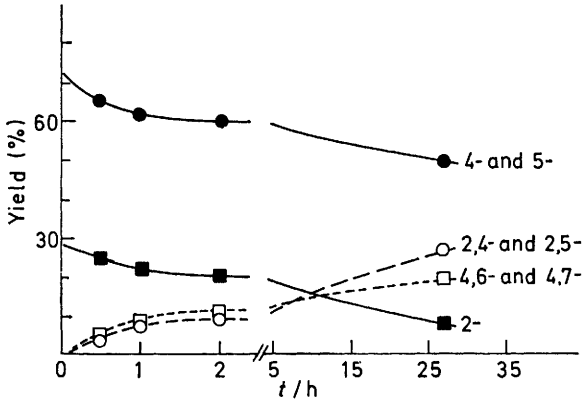


FIGURE 1 Variation of the composition of the sulphonic acid mixture resulting from 1-methylnaphthalene in 90.1% H_2SO_4 at 25 °C with reaction time

the 2,4- and 4,7-disulphonic acids is directly apparent from the ^{1}H n.m.r. spectrum of the sulphuric acid reaction mixture. The two disulphonic acid components were isolated by fractional crystallization. The additional presence of characteristic 5-H signal at δ 9.46 (98.4% H_2SO_4) and 9.55 (D_2O); its methyl signal was found as a shoulder at δ 3.14 (98.4% H_2SO_4). The ^{1}H n.m.r. data of the four disulphonic acids formed are listed in Table 1. The disulphonic acid isomer distribution was obtained by ^{1}H n.m.r. analysis [22] of the D_2O solution obtained from the original reaction mixture to be 22% 2,4-, 22% 2,5-, 9% 4,6-, and 47% 4,7-disulphonic acid.

The sulphonation of potassium 1-methylnaphthalene-4-sulphonate was also studied. The isomer distributions are given in Table 2.

Sulphonation with 110% H_2SO_4: *Trisulphonic Acids.*—Trisulphonation of 1-methylnaphthalene was effected with 110% H_2SO_4 at 25 °C. The ^{1}H n.m.r. spectrum of the resulting solution showed the presence of one major product (76%), *viz.* 1-methylnaphthalene-2,4,7-trisulphonic acid. The minor components were assigned to be the 2,4,6- (16%) and 2,5,7-trisulphonic acids (8%). The ^{1}H n.m.r. assignment of the 2,4,7-isomer was supported by the observation that sulphonation of 1-methylnaphthalene-4-, -2,4-di-, and -4,7-di-sulphonate each with 110% H_2SO_4 resulted in formation of the same product. With the 4-monosulphonic acid only a second product was obtained, the 2,4,6-trisulphonic acid. The 2,5,7-isomer was only obtained from 1-methylnaphthalene; it was recognized by its low field 8-H signal at δ 9.81. Supporting evidence for the correct assignment of the 1-methylnaphthalene-2,4,6- and -2,4,7-trisulphonic acids comes from a comparison with the naphthalene-2,4,6- and -2,4,7-trisulphonic acids, the ^{1}H n.m.r. data

TABLE 1

^{1}H N.m.r. data of naphthalenesulphonic acids [a]

Substituted naphthalene	Solvent	Chemical shift (δ) 1	2	3	4	5	6	7	8
1-Me-2-SO_3H	90% H_2SO_4	2.93		8.36	7.1—8.3 [b]				
1-Me-2-SO_3^-	D_2O	3.04		8.12	7.0—7.9 [b]				
1-Me-4-SO_3H	90% H_2SO_4	2.55	7.23	8.17		8.52	7.4—8.0 [b]		
1-Me-4-SO_3^-	D_2O	2.22	7.05	8.13		8.92	7.3—7.9 [b]		
1-Me-5-SO_3H	90% H_2SO_4	2.55	unr.	unr.	unr.	unr.	unr.	unr.	unr.
1-Me-5-SO_3^-	D_2O	2.27	7.2 [c]	7.6 [c]	8.77		8.32	7.6 [c]	7.6 [c]
1-Me-2,4-$(SO_3H)_2$	95% H_2SO_4	3.48		9.1		9.1	7.8—9.0 [b]		
1-Me-2,4-$(SO_3^-)_2$	D_2O	3.26		9.10		9.00	7.4—8.1 [b]		8.11
1-Me-2,5-$(SO_3^-)_2$	D_2O	3.43		8.55	9.09		8.5 [c]	7.95	8.5 [c]
1-Me-4,7-$(SO_3H)_2$	95% H_2SO_4	3.17	7.94	8.7		9.1	7.9 [c]		8.6
1-Me-4,7-$(SO_3^-)_2$	D_2O	2.58	7.23	8.33		9.25	8.52		8.71
1-Me-4,6-$(SO_3H)_2$	95% H_2SO_4	3.15	7.94	7.9 [c]		9.46		7.8—9.0 [b]	
1-Me-4,6-$(SO_3^-)_2$	D_2O	2.47	7.1—8.6 [b]			9.55		7.1—8.6 [b]	
1-Me-2,4,6-$(SO_3H)_3$	110% H_2SO_4	3.71		9.4 [c]		9.8		8.8 [c]	8.8 [c]
1-Me-2,4,6-$(SO_3^-)_3$	D_2O	3.54		unr.		9.65		unr.	unr.
1-Me-2,4,7-$(SO_3H)_3$	110% H_2SO_4	3.71		9.41		9.34	8.84		9.60
1-Me-2,4,7-$(SO_3^-)_3$	D_2O	3.58		9.16		9.30	8.59		9.29
1-Me-2,5,7-$(SO_3H)_3$	110% H_2SO_4	3.68		unr.	unr.		unr.		9.81
2,4,6-$(SO_3H)_3$	110% H_2SO_4	9.50		9.30		9.69		8.76	8.99
2,4,6-$(SO_3^-)_3$	D_2O	9.04		8.97		8.63		8.46	8.69
2,4,7-$(SO_3H)_3$	110% H_2SO_4	9.4 [c]		9.4 [c]		9.4 [c]	8.8		9.4 [c]
2,4,7-$(SO_3^-)_3$	D_2O	9.14		8.99		9.28	8.60		9.07

[a] Unr. = unresolved; coupling constants $J_{\alpha,\beta}$ and $J_{\beta,\beta'}$ are 8—10 and $J_{\alpha,\beta'}$ 1—2 Hz. [b] Unresolved multiplets in between the quoted chemical shifts. [c] Centre of unresolved multiplet.

1-methylnaphthalene-2,5-disulphonic acid was revealed from the ^{1}H n.m.r. spectrum in D_2O of the potassium sulphonate mixture obtained upon carefully working up a sulphuric acid reaction mixture and confirmed by the double resonance technique. The presence of 1-methylnaphthalene-4,6-disulphonic acid was apparent from its of which are also listed in Table 1. For the two sets of homologues the characteristic absorption of 5-H is comparable.

[22] (*a*) H. Cerfontain, A. Koeberg-Telder, C. Kruk, and C. Ris, *Analyt. Chem.*, 1974, **46**, 72; (*b*) A. Koeberg-Telder, C. Ris, and H. Cerfontain, *J.C.S. Perkin II*, 1974, 98.

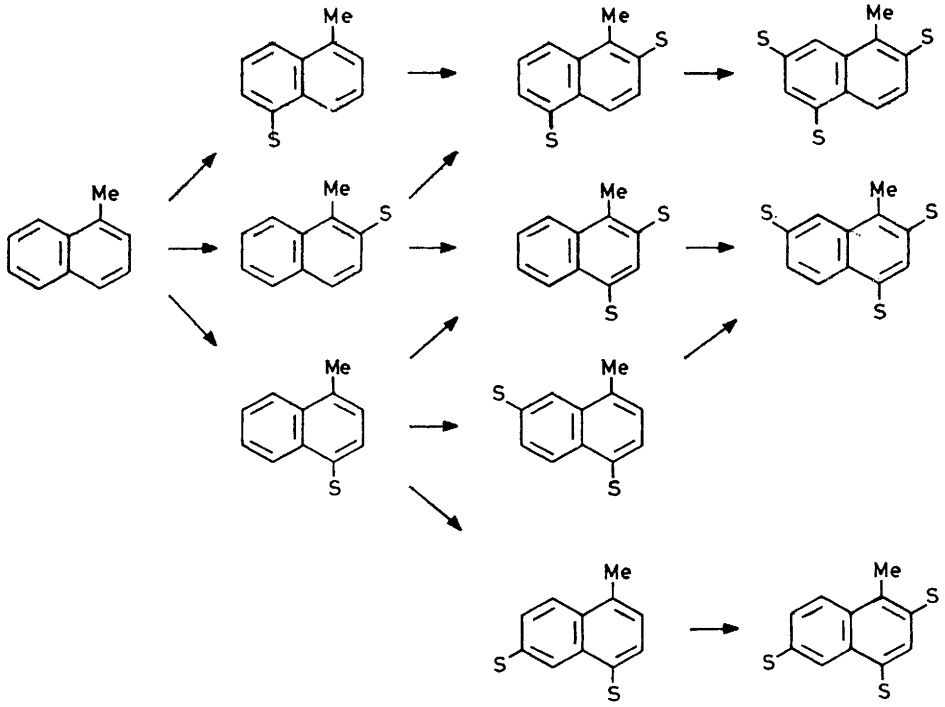
Sulphonation with SO_3 *in Nitromethane.*—Treatment of 1-methylnaphthalene with 0.9 equiv. SO_3 in nitromethane at 0 and 12 °C yielded exclusively 1-methylnaphthalene-4-sulphonic acid. Using three equiv. SO_3 at 12 °C 1-methylnaphthalene was converted (92%) into a mixture of the 2,4-, 4,6-, and 4,7-disulphonic acids. The isomer distributions for the SO_3 disulphonation of 1-methylnaphthalene and its 4-sulphonic acid are listed in Table 2.

TABLE 2

Isomer distribution in the sulphonation of 1-methylnaphthalene and some sulphonic acid derivatives

Substituted naphthalene	Reagent [a]	Sulphonic acid isomer distribution (%)									
		2-	4-	5-	2,4-	2,5-	4,6-	4,7-	2,4,6-	2,4,7-	2,5,7-
1-Me	90.1% H_2SO_4	25	60	15							
	98.4% H_2SO_4				22	22	9	47			
	110% H_2SO_4								16	76	8
	1 equiv. SO_3 in $MeNO_2$		>95								
	3 equiv. SO_3 in $MeNO_2$				53		5	42			
1-Me-4-SO_3H	95.0% H_2SO_4				30		10	60			
	98.4% H_2SO_4				24		11	65			
	110% H_2SO_4								16	84	
	3 equiv. SO_3 in $MeNO_2$				56		3	41			
1-Me-2,4-$(SO_3H)_2$	110% H_2SO_4									95	
1-Me-4,7-$(SO_3H)_2$	110% H_2SO_4									95	
2,6-$(SO_3H)_2$	110% H_2SO_4								95		
2,7-$(SO_3H)_2$	110% H_2SO_4									95	

[a] The temperature for sulphonation with sulphuric acid is 25 °C, whereas that for SO_3 in nitromethane is 12 °C.



SCHEME; S = SO_3H

DISCUSSION

The overall sequence for the sulphonation of 1-methylnaphthalene in sulphuric acid based on the present results is presented in the Scheme.

Monosulphonic Acid Formation.—The isomer distribution of the monosulphonic acids changes with increasing sulphuric acid concentration over the acid range 90—110% H_2SO_4, as will be outlined. In 90% sulphuric acid the ratio of the monosulphonic acids is 2 : 4 : 5 = 25 : 60 : 15 (Table 2). The isomer distribution of the disulphonic acids, calculated using the isomer distributions for the monosulphonation of 1-methylnaphthalene in 90% H_2SO_4 and of 1-methylnaphthalene-4-sulphonic acid in 95% H_2SO_4 and considering that the 2- and 5-sulphonic acids only yield the 2,4- and 2,5-disulphonic acids (Scheme), was found to be (2,4 + 2,5) : 4,6 : 4,7 = 58 : 6 : 36, *i.e.* significantly different from that actually observed (see Table 2). Apparently in the initial sulphonation of 1-methylnaphthalene in 98.4% H_2SO_4 the relative amount of either the 2- or the 5-sulphonic acid is (or both are) less than presumed. Actually it is

mainly the 2-isomer, as will now be demonstrated. In 98.4% H_2SO_4 the relative amount of 2,4-disulphonic acid resulting from 1-methylnaphthalene is 22% and the amount of that acid obtained upon sulphonation of 1-methylnaphthalene-4-sulphonic acid is 24%. In view of the *mono*sulphonic acid isomer distribution in 90.1% H_2SO_4 it can be inferred that the 2,4-disulphonic acid obtained in the disulphonation of 1-methylnaphthalene results predominantly from the 4-sulphonic acid.

The amount of 2,5-disulphonic acid obtained in the sulphonation of 1-methylnaphthalene in 98.4% H_2SO_4 is

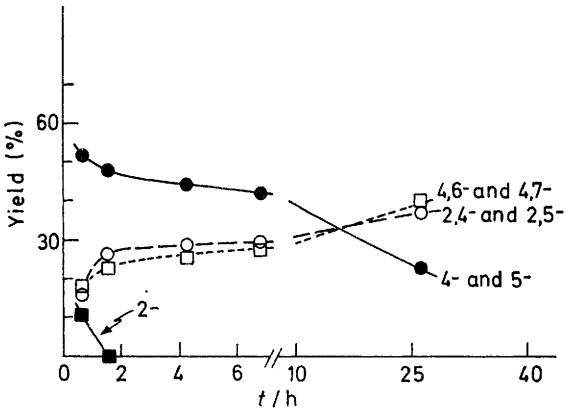


FIGURE 2 Variation of the composition of the sulphonic acid mixture resulting from 1-methylnaphthalene in 95.0% H_2SO_4 at 25 °C with reaction time

22% (Table 2). This acid results from the 2- and 5-monosulphonic acids (Scheme) and if the isomer distribution for the monosulphonation of 1-methylnaphthalene in 98.4% H_2SO_4 would be the same as observed in 90.1% sulphuric acid, then the formation of the 2,5-disulphonic acid would be at most 32 [= 25 — (22 — 60 × 0.24) + 15]%. It is highly improbable that this diacid is formed largely from the 2-sulphonic acid. Figure 2 shows that 1-methylnaphthalene-2-sulphonic acid is far more reactive towards sulphonation than its isomers, illustrating that for this sulphonic acid the deactivation by the sulphonic acid substituent is strongly reduced.*

Since 1-methylnaphthalene-4-sulphonic acid gives 24% of substitution in the sulpho-carrying ring (*i.e.* formation of 2,4-disulphonic acid), it is to be expected that 1-methylnaphthalene-2-sulphonic acid, because of its reduced deactivation towards electrophilic substitution, would yield at least a similar degree of substitution in the same ring and accordingly only a limited amount of the 2,5-disulphonic acid. This isomer thus largely results from the 5-sulphonic acid. Hence it follows that the degree of 2-substitution in the monosulphonation of 1-methylnaphthalene is lower for 98.4% than for 90.1% H_2SO_4.† This point deserves further comment.

It was demonstrated that for sulphonation in sulphuric acid, different mechanisms operate depending on the acid concentration.[24] In sulphuric acid of low acid strength (75—80%) the electrophilic entity is $H_3SO_4^+$, whereas at higher acid strength (95—99%) it is $H_2S_2O_7$.[4a] In the intermediate region (80—95% H_2SO_4) a gradual changeover in mechanisms takes place. The acid concentration at which both mechanisms are equally important depends on the reactivity of the position to be substituted and the steric hindrance to be encountered. The isomer distribution for the sulphonation of *e.g.* polyalkylbenzenes is dramatically different for both mechanisms.[25-27] Some characteristic data are listed in Table 3. For all the methylbenzenes the degree of sulphonation at the sterically most hindered position increases with increasing sulphuric acid concentration. At first sight this seems rather surprising as one expects with a bulkier reagent an increase in steric repulsion. However, the activation entropy data show that the $H_3SO_4^+$ mechanism is more subject to steric hindrance than the $H_2S_2O_7$ mechanism.[26] This was explained in terms of a shorter distance between the incoming SO_3H^+ group and the reaction centre (and thus to the adjacent methyl group) in the transition state leading to the σ-complex for $H_3SO_4^+$ as electrophile than for $H_2S_2O_7$. This indicates that the

TABLE 3

Sulphonation of methyl substituted benzenes [a]

Substituted benzenes	Isomer distribution (%) $H_3SO_4^+$ mechanism	Isomer distribution (%) $H_2S_2O_7$ mechanism	Ref.
1-Me	2- 21.2; 3- 2.1; 4- 76.7	2- 45.5; 3- 5.2; 4- 49.3	24
1,2-Me_2	3- 6.5; 4- 93.5	3- 45.1; 4- 54.9	25
1,3-Me_2	2- 0.5; 4- 98.9; 5- 0.6	2- 14.5; 4- 84.3; 5- 1.2	25
1,2,3-Me_3	4- 86; 5- 14	4- 90; 5- 10	26
1,2,4-Me_3	5- 89; 6- 11	5- 75; 6- 25	26

[a] The first datum gives the position of substitution, the second the relative amount (%) of isomer formed.

* This may be explained in terms of hyperconjugative electron release by the adjacent methyl substituent,[23-25] and possible in addition by steric repulsion between the adjacent methyl and sulpho-groups.

† On the assumptions that for 98.4% H_2SO_4 the rates of formation of the 2,4- and 2,5-disulphonic acids from the 2-monosulphonic acid are about equal and that the degree of formation of the 5-sulphonic acid is the same as observed for 90.1% H_2SO_4 (see however later), it can be calculated that the degree of the initially formed 2-sulphonic acid in 98.4% H_2SO_4 is *ca.* 8%.

[23] A. J. Prinsen, A. Koeberg-Telder, and H. Cerfontain, *Tetrahedron*, 1970, **26**, 1953.
[24] C. W. F. Kort and H. Cerfontain, *Rec. Trav. chim.*, 1968, **87**, 25.
[25] H. Cerfontain, F. L. J. Sixma, and L. Vollbracht, *Rec. Trav. chim.*, 1963, **82**, 559.
[26] A. J. Prinsen and H. Cerfontain, *Rec. Trav. chim.*, 1969, **88**, 833.
[27] H. Cerfontain, A. Koeberg-Telder, C. Ris, and Z. R. H. Schaasberg-Nienhuis, *J.C.S. Perkin II*, 1975, 970.

$H_2S_2O_7$ sulphonation has an 'earlier' and that the $H_3SO_4^+$ has a 'later' transition state. According to the Hammond [28] principle the site of attack for the $H_2S_2O_7$ mechanism should then be more influenced by the electron densities of the various positions of the substrate, whereas the position of substitution by the $H_3SO_4^+$ mechanism should be more governed by the localisation energies of the different positions of the molecule.

In order to test this prediction, simple Hückel MO calculations were performed for the methylbenzenes based on the inductive model using k' 0.3.[29,*] The numerical data are in Table 4. They are in line with the conclusion drawn before on the difference in nature of the transition states for the $H_3SO_4^+$ and $H_2S_2O_7$ mechanisms. With 1,2,4-trimethylbenzene there is no sulphonation at the 3-position.[27] Similarly, the degree of 2-substitution with *m*-xylene [25] is smaller than expected on the basis of the MO calculations. Both these differences may be explained in terms of a buttressing effect upon forming the arenesulphonic acid from the preceding σ-complex, this effect being stronger with the 1,2,4-trimethylbenzene than *m*-xylene because of the additional adjacent methyl group.

As to 1-methylnaphthalene, from a comparison of the electron densities with the localisation energies obtained by simple Hückel MO calculations (Table 5), it is to be expected that the degree of 2-substitution is higher for the $H_2S_2O_7$ than the $H_3SO_4^+$ mechanism. The actual results, however, are just the opposite (*cf.* the results for 90 and 95% H_2SO_4 of Table 1). This may be explained in terms of an enhanced steric repulsion for *ortho*-substitution with 1-methylnaphthalene as compared with toluene, as a result of the shorter C(1)–C(2) bond length (1.395 Å in benzene [31a,b] *versus* 1.361 Å in naphthalene [31c]). The incoming $H_2S_2O_7$ group may thus encounter a larger steric repulsion from the methyl substituent as a result of its closer proximity in 1-methylnaphthalene than in toluene. This effect seems to overrule the difference in isomer distribution as a result of the differences in C(2) · · · S bond distance in the transition state leading to substitution at the 2-position for the $H_3SO_4^+$ and $H_2S_2O_7$ types of sulphonation, as observed in toluene.

The same effect as to the 2-substitution is observed for the monosulphonation of 1-methylnaphthalene with 110% H_2SO_4 which is apparent from a comparison with 1-methylnaphthalene-4-sulphonic acid in 110% H_2SO_4 (Table 2). The electrophilic entity for this sulphonation is $H_2S_4O_{13}$,[4a] which because of enhanced steric hindrance apparently does not lead to initial 2-substitution and by comparison with the entities $H_3SO_4^+$ and $H_2S_2O_7$ will have a still 'earlier' transition state than $H_2S_2O_7$. Accordingly, the reaction path will follow the reactivity order indicated by the electron densities more precisely. Thus a reduced substitution at the 5-position is to be expected which is in fact observed by the low yield of 1-methylnaphthalene-2,5,7-trisulphonic acid (8%).

In the sulphonation of 1-methylnaphthalene with 1 equiv. SO_3 in nitromethane as complexing solvent the 4-sulphonic acid is the only product.

Disulphonic Acid Formation.—Upon disulphonation of 1-methylnaphthalene under various conditions two main products are formed, the 2,4- and 4,7-disulphonic acids. The substantial formation of the 2,4-isomer is remarkable, as it is common for electron-withdrawing substituents to deactivate the ring to which they are attached more strongly than the other, and thus that substitution occurs at the most reactive (*i.e.* the α-)

TABLE 4

MO Calculations of methyl substituted benzenes [a]

	1-Me		1,2-Me_2		1,3-Me_2		1,2,3-Me_3		1,2,4-Me_3	
	δq	L	δq	L	δq	L	δq	L	δq	L
1	−119	2.5360	−73	2.4290	−121	2.5367	−74	2.4343	−43	2.3401
2	+47	2.4290	−73	2.4290	+94	2.3383	−25	2.3383	−76	2.4235
3	−3	2.5367	+45	2.4343	−121	2.5367	−74	2.4343	+91	2.3417
4	+30	2.4372	+28	2.4315	+77	2.3401	+74	2.3434	−91	2.4315
5	−3	2.5367	+28	2.4315	−6	2.5371	+25	2.4253	+76	2.3269
6	+47	2.4290	−45	2.4343	+77	2.3401	+74	2.3434	+43	2.4283

[a] q is the electron density in 10^3 electron units; L is the localization energy in units of β.

TABLE 5

MO Calculation of 1-methylnaphthalene

Parameter [a]	Position 1	2	3	4	5	6	7	8
δq	−132	+63	−5	+41	+7	−2	+10	−8
L	2.2985	2.3289	2.1483	2.1926	2.2708	2.4802	2.4408	2.3007

[a] See subscript at Table 4.

* CNDO/2 Calculations have been performed,[30] but they hardly differ from our simple Hückel MO calculations.

[28] G. S. Hammond, *J. Amer. Chem. Soc.*, 1955, **77**, 334.

[29] E. L. Mackor, G. Dallinga, J. H. Kruizinga, and A. Hofstra, *Rec. Trav. chim.*, 1956, **75**, 836.

[30] N. S. Isaacs and D. Cvitas, *Tetrahedron*, 1971, **27**, 4139.

[31] Tables of Interatomic Distances and Configuration in Molecules and Ions, Chem. Soc. Special Publication, (*a*) No. 11, 1958, p. M196; (*b*) No. 18, 1965, p. M127s; (*c*) *ibid.*, p. M154s.

positions of the other ring.[32a] This is in fact observed in the sulphonation of 1-nitronaphthalene and various 1-sulphonaphthalenes.[32b] With 1-methylnaphthalene the situation is complicated, as sulphonation of 1-methylnaphthalene-4-sulphonic acid at an α-position does not occur as a result of the steric repulsion for the *peri*-substitution. With the corresponding 2-sulphonic acid, substitution at an α-position, *viz.* the 4- and 5-position is possible, but there the situation is different as a result of the adjacent methyl and sulpho-groups which diminishes the deactivating effect of the sulpho-group.

The main product in the sulphonation of 1-methylnaphthalene-4-sulphonic acid by the $H_2S_2O_7$ mechanism is the 4,7-disulphonic acid (60—65%). The amount of 2,4-disulphonic acid is smaller in sulphonation with 95% H_2SO_4 (*i.e.* by the $H_2S_2O_7$ mechanism) than with SO_3 in nitromethane as solvent. This may be explained in terms of a higher degree of steric hindrance with the former than the latter type of sulphonation which proceeds by a different mechanism.[4b]

Trisulphonic Acid Formation.—For all the disulphonic acids obtained upon sulphonation of 1-methylnaphthalene the number of relatively still reactive substrate positions is one. The 2,4- and 4,7-disulphonic acids both give 1-methylnaphthalene-2,4,7-trisulphonic acid as the only product, whereas the 4,6-isomer gives the 2,4,6-isomer. It cannot be excluded that some 2,4,6-trisulphonic acid originates from the 2,4-disulphonic acid. Evidently the 2,5,7-isomer is formed from the 2,5-disulphonic acid.

From the ^{1}H n.m.r. spectra of the trisulphonic acids one peculiar observation attracts attention. The 8-H signal of the 2,4,7-isomer is at lower field (δ 9.60) than that of 3-H, which is in between the two sulphonic acid groups (δ 9.41). This may be explained in terms of both steric and electronic effects, as suggested before with *e.g.* the polymethylbenzenesulphonic acid(s).[33]

EXPERIMENTAL

Materials.—*Potassium 1-methylnaphthalene-2,4- and -4,7-disulphonate.* The homogeneous mixture obtained upon sulphonating 1-methylnaphthalene (2.5 g) in 95% H_2SO_4 (35 ml) at 25 °C afforded a precipitate. Filtration after a week and subsequent neutralization of the residue with KOH in water, removal of the solvent, and subsequent continuous extraction with ethanol afforded 1-methylnaphthalene-2,4-disulphonate. Addition of the filtrate to an appropriate amount of ice–water resulted in a second precipitate. This afforded, after work-up, 1-methylnaphthalene-4,7-disulphonate. For the ^{1}H n.m.r. data see Table 1.

Potassium 1-methylnaphthalene-4-sulphonate. SO_3 (1 ml) in nitromethane (20 ml) was added over 15 min at 0 °C to a solution of 1-methylnaphthalene (3.1 g) in CH_3NO_2 (20 ml). After 30 min water (20 ml) was added and the resulting mixture heated to 50 °C. The water layer was separated, extracted with CH_2Cl_2, neutralized with KOH, and after removal of the solvent the sulphonate was obtained. For ^{1}H n.m.r. data see Table 1.

Sulphonation Procedure.—Sulphonation with sulphuric acid was performed by adding sulphuric acid (1 ml) of known concentration to the aromatic substrate (10.5 mmol) at 25 °C and shaking of the resulting mixture to homogeneity. The progress of the reaction was followed by examining the sulphuric acid solution directly by ^{1}H n.m.r., except for the fuming sulphuric acid solutions which were first freed from the excess of SO_3. The sulphonates were obtained by quenching the sulphuric acid solutions in ice–water. After neutralizing with KOH, the solvent was removed and the resulting material extracted with ethanol.

The sulphonation of 1-methylnaphthalene with SO_3 was performed by dropwise addition with stirring under dry nitrogen of SO_3 (0.9 and 3 equiv. respectively) in nitromethane to the substrate (0.3 g) in CH_3NO_2 (5 ml) at 0 or 12 °C. After 1 h D_2O (1—2 ml) was added, and the solution heated in order to hydrolyse any (solid) anhydrides. After cooling the D_2O layer was separated, washed with CH_2Cl_2, and nitrogen was bubbled through for 30 min. The D_2O solutions were analysed by ^{1}H n.m.r.

^{1}H *N.m.r. Analyses.*—The structural assignments of the products were based on ^{1}H n.m.r. analyses. The compositions of the reaction mixtures were determined by multicomponent ^{1}H n.m.r. analyses, [22] with use of the double resonance technique. The ^{1}H n.m.r. data are given in Table 1. The assignments were based on substituent shielding parameters, signal area ratios, and coupling constants. The spectra were recorded with Varian HA 100 and XL 100 spectrometers, using tetramethylsilane as an external standard.

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[32] H. Cerfontain, 'Mechanistic Aspects in Aromatic Sulfonation and Desulfonation,' Interscience, New York, 1968, (*a*) p. 70; (*b*) ch. 9.

[33] H. Cerfontain, A. Koeberg-Telder, and C. Ris, to be published.