Aromatic Sulphonation. Part XLVI.[1] Isomer Distributions in the Sulphonation of Acenaphthene and its 3- and 5-Sulphonic Acids with Sulphuric Acid

By **Hans Cerfontain** * and **Zwaantje R. H. Schaasberg-Nienhuis**, Laboratory for Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, Amsterdam, The Netherlands

The sulphuric acid sulphonation of acenaphthene and its mono- and di-sulphonic acids has been investigated. The kinetic isomer distribution for sulphonation in 95·2% H_2SO_4 at 25° is for acenaphthene 68 ± 14% 3- and 32 ± 14% 5-substitution, for acenaphthene-3-sulphonic acid 6 ± 2% 5-, 66 ± 4% 6-, and 28 ± 3% 8-substitution, and for acenaphthene-5-sulphonic acid 28 ± 3% 3- and 72 ± 3% 8-substitution. The relatively high degree of substitution adjacent to the ethylene bridge is explained in terms of an electrostatic proximity effect. The pseudo-first-order rate constants for sulphonation of the 3,5-, 3,6-, and 3,8-disulphonic acids in the reaction mixtures, *i.e.* in *ca.* 94% H_2SO_4, at 25° are (6 ± 2) × 10^3, (1·9 ± 0·2) × 10^3, and (2·4 ± 0·3) × 10^3 s^{-1}, respectively.

THE electrophilic substitution of acenaphthene has received renewed attention in the last decade.[2] However, no reports on its sulphonation have appeared since 1933.[3] It has been reported[4] that acenaphthene on treatment with concentrated sulphuric acid at 100° yields the 5-sulphonic acid, but it was argued later[5] that this assignment was erroneous, and that the product was instead the 3-isomer. Acenaphthene with chlorosulphuric acid in nitrobenzene at 0° yields 75% of another sulphonic acid[4] which was considered originally[4] to be the 3-isomer, but later,[5] conversely, the 5-isomer. According to this second[5] assignment, the sulphonation behaviour of acenaphthene seems to be similar to that of naphthalene[6] in that, at low temperatures, *i.e.* under conditions of kinetic control, mainly the α-substitution product is formed, whereas at high temperatures the thermodynamically more stable β-product is obtained.

Connected with sulphonation studies of some reduced benzocycloalkenes,[7] and in view of the conflicting assignments of the acenaphthenemonosulphonic acids, it was thought of interest to re-study the sulphonation of acenaphthene and its 3- and 5-sulphonic acids.

RESULTS AND DISCUSSION

All sulphonations were carried out in a large excess of sulphuric acid.

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TABLE 1

^{1}H N.m.r. data of acenaphthene and its sulphonic acids

Substituents	Solvent	δ H-1	H-2	H-3	H-4	H-5	H-6	H-7	H-8	J_{nm}/Hz 1,8	3,4	4,5	6,7	6,8	7,8
	$CDCl_3$	3·24		7·02	7·22	7·37									
a	CCl_4	3·24		7·11	7·31	7·46				1·5	6·7	8·1		1·2	
3-SO_3^-	D_2O	3·04—3·26 (m)	3·38—3·60 (m)		7·72	7·51—7·2		7·4—7·09		1·2		8·7			7
3-SO_3H	90·0% H_2SO_4	3·6br (s)	>3·6 [b]												
5-SO_3^-	D_2O	2·94br (s)	2·94br (s)	7·38	7·93		8·15	7·54	7·17	1·8	7·2		8·4		7·3
5-SO_3H	90·0% H_2SO_4	3·3br (s)	3·3br (s)												
3,5-$(SO_3^-)_2$ [c]	D_2O				8·43		8·17	7·76	7·11						
3,5-$(SO_3H)_2$	95·2% H_2SO_4	3·6	3·9		8·58 [d]		8·34 [d]	7·88 [d]	7·57 [d]				8·5		7·5
3,6-$(SO_3^-)_2$	D_2O	3·1—3·3	3·5—3·7		8·10	8·42		8·11	7·23	1·9		9·0			7·5
3,6-$(SO_3^-)_2$ [c]	D_2O				8·04	8·29		8·05	7·24			9·0			7·5
3,6-$(SO_3H)_2$	95·2% H_2SO_4	3·68br (m)	3·83br (m)		8·17	8·40		8·51	7·73			9·0			7·5
3,8-$(SO_3^-)_2$ [c]	D_2O				7·84	7·53									
3,8-$(SO_3H)_2$	95·2% H_2SO_4	3·89 [d]			8·07 [d]	7·88 [d]						8·8			
5,6-$(SO_3^-)_2$ [c]	D_2O	2·94		7·19	8·25										
5,6-$(SO_3H)_2$ [c]	95·2% H_2SO_4	3·3		7·7	8·7										
3,5,8-$(SO_3H)_3$	95·2% H_2SO_4	4·43br (s)	4·43br (s)		8·84		8·58	8·44					8·8		

[a] M. J. S. Dewar and R. C. Fahey, *J. Amer. Chem. Soc.*, 1963, **85**, 2704. [b] The sulphonation of the 3-sulphonic acid is so fast that its H-2 absorption cannot be observed, as it is obscured by the disulphonic acid methylene absorptions. [c] Chemical shifts calculated on the basis of additivity of substituent shifts;[8] note that the agreement between the calculated and observed chemical shifts for the 3,6-disulphonate is satisfactory. [d] See text.

TABLE 2

Products of sulphonation of acenaphthene and its sulphonic acids in an excess of sulphuric acid at 25°

Substrate (weight % relative to H_2SO_4)		H_2SO_4 (%)	Time (h)	Sulphonation products (%) * 3-	5-	3,5-di-	3,6-di-	3,8-di-	3,5,8-tri-
Acenaphthene-3-sulphonic acid	(2)	95·2	0·42	6 ± 2		5 ± 2	63 ± 4	27 ± 3	0
	(4)	95·2	1·22	4 ± 2		7 ± 2	62 ± 4	26 ± 3 (24 ± 4)	⩽2
	(4)	95·2	5·9	0		7 ± 2	62 ± 4	21 ± 3 (21 ± 4)	9 ± 1 (11 ± 1)
	(4)	95·2	27	0		2 ± 1	55 ± 4 (57 ± 4)	18 ± 3 (17 ± 4)	27 ± 2 (26 ± 2)
	(4)	95·2	168	0		0	16 ± 4 (18 ± 4)	5 ± 2 (4 ± 2)	81 ± 3 (75 ± 3)
		95·2	408				3 ± 1	<1	97 ± 2
Acenaphthene-5-sulphonic acid	(2)	95·2	0·35		14 ± 3	21 ± 3	65 ± 4	0	0
	(5)	95·2	0·73		11 ± 3	27 ± 3	60 ± 4	0	2
	(5)	95·2	6·2		0	23 ± 3	70 ± 4	0	8 ± 1 (10 ± 1)
	(5)	95·2	29		0	15 ± 3	59 ± 4	0	27 ± 2 (26 ± 2)
	(5)	95·2	168		0	<2	27 ± 3	0	71 ± 3 (69 ± 3)
	(5)	95·2	408		0	0	6 ± 2	0	94 ± 2
Acenaphthene	(2)	80·9	240			17 ± 3	69 ± 4	13 ± 2 (12 ± 3)	⩽2
	(5)	90·0	72			18 ± 3	53 ± 4	17 ± 3 (14 ± 3)	13 ± 1 (15 ± 2)
	(2)	95·2	1·0			15 ± 3	61 ± 2	17 ± 3	8 ± 2
	(4)	95·2	1·0			16 ± 3	57 ± 2	21 ± 3	6 ± 2
	(1·5)	98·0	2·0			9 ± 2	39 ± 3	17 ± 3	35 ± 2 (36 ± 3)
	(3)	98·0	2·0			14 ± 2	47 ± 3	14 ± 3	26 ± 2 (28 ± 2)
	(5)	98·0	2·0			11 ± 2	53 ± 4	16 ± 3	21 ± 2 (20 ± 2)
	(1·5)	98·0	24			0	3 ± 2	0	97 ± 2 (97 ± 3)
	(5)	98·0	24			<2	22 ± 3	7 ± 2	70 ± 3 (69 ± 2)
	(4)	103	24						⩾98

* The data in parentheses refer to the analysis from the aliphatic proton n.m.r. signals.

The ^1H n.m.r. spectra of the final reaction mixtures obtained from treatment of each of acenaphthene, acenaphthene-3- and -5-sulphonic acid, and acenaphthene-3,6-disulphonic acid with 90—103% H_2SO_4 at 25° are all identical. They exhibit a broad aliphatic singlet and an aromatic ABX absorption (Table 1) in an integrated ratio of 4 : 0·96 : 0·96 : 0·92. These absorptions are ascribed to acenaphthene-3,5,8-trisulphonic acid.

The compositions of the reaction mixtures at intermediate reaction times (Table 2) were determined by multi-component n.m.r. analysis[8] of, independently, the aromatic and the aliphatic absorptions, using the chemical shift data listed in Table 2. The exclusive formation of the 3,5,8-trisulphonic acid eliminates the occurrence of the 5,6-disulphonic acid as a possible intermediate in kinetically controlled sulphonations. It was further assumed that sulphonation occurs only at the 3-(or 8-), and 5-(or 6-)positions which are in fact the activated positions for electrophilic substitution.

The assignment of the aromatic hydrogen absorptions of the 3,5- and 3,8-disulphonic acid was based in part on a comparison of the absorptions observed in the reaction mixtures with the chemical shifts of the corresponding sulphonates, as calculated on the basis of additivity of substituent shifts[8] and further on the observations that the absorptions of the 3,5-isomer were present in the spectra of the mixtures resulting from both the 3- and the 5-sulphonic acid, whereas those of the 3,8-isomer were only found in the spectra of the mixtures resulting from the 3-sulphonic acid.

The assignments of the methylene hydrogen atoms also deserve some discussion. On starting with the 5-sulphonic acid the original broad singlet is replaced by two absorptions of equal intensity at somewhat lower field which are eventually replaced by the broad singlet of the 3,5,8-trisulphonic acid at still lower field. The two absorptions of equal intensity are assigned to both 3,5- and 3,6-disulphonic acid, as the 3,6-disulphonic acid is known to exhibit such an absorption pattern (Table 1).

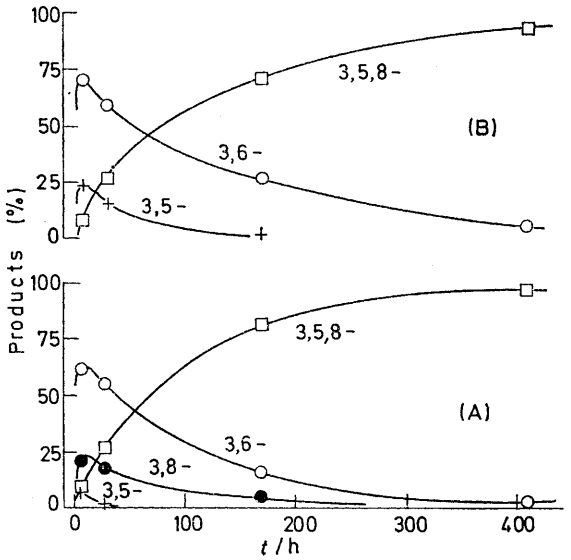
Upon reaction of the 3-sulphonic acid, the original two methylene absorptions of equal intensity are replaced by two absorptions at somewhat lower field, of which the lower of these has the higher intensity. Since the two methylenes of the 3,5-disulphonic acid exhibit the same chemical shifts as those of the 3,6-isomer (*vide supra*), the higher intensity of the low field signal must be due to a singlet absorption which can only be attributed to the 3,8-disulphonic acid. Moreover, the aromatic n.m.r. absorption of the reaction mixture does contain the required AB pattern.

Sulphonation of acenaphthene-5-sulphonic acid leads to the initial formation of the 3,5- and 3,6-disulphonic acid which are eventually both converted into the 3,5,8-trisulphonic acid. The initial ratio of the 3,5- and 3,6-isomers is 0·39 ± 0·06. The variation in the isomer ratio with time (Figure) shows that sulphonation is faster for the 3,5- than for the 3,6-isomer.

Sulphonation of the 3-sulphonic acid yields the 3,5-, 3,6-, and 3,8-disulphonic acids. The initial isomer distribution is 6 ± 2% 3,5-, 66 ± 4% 3,6-, and 28 ± 3% 3,8-isomer. The variation of the disulphonic isomer ratio with time (Figure) reveals that the rate of sulphonation of the 3,5-isomer exceeds those of the 3,6- and 3,8-isomer.

The further sulphonation of the disulphonic acids in 95% H_2SO_4 (Figure) was found to follow first-order kinetics, with $10^3{}_{ps}k_1$ (25°) for the 3,5-, 3,6-, and 3,8-isomers being 5·4 ± 1·8 and 12 ± 7; 2·1 ± 0·2 and 1·7 ± 0·2; and 2·4 ± 0·3 s^{-1} respectively. The first of the two data refers to the experiments with acenaphthene-3-sulphonic acid as substrate and the second to those with the 5-sulphonic acid.

Acenaphthene, upon shaking with an excess of sulphuric acid, dissolves only very slowly; *e.g.* 4%



Reaction of acenaphthene-3-sulphonic acid (A) and acenaphthene-5-sulphonic acid (B) with 95·2% H_2SO_4 at 25° (+ = 3,5-, ○ = 3·6-, and ● = 3,8-disulphonic acid; □ = 3,5,8-trisulphonic acid)

acenaphthene added to sulphuric acid required 0·35 h. No 3- or 5-sulphonic acid was, however, found in analysis within the limits of detection (*i.e.* 3%), not even directly after the substrate had been dissolved. Accordingly the rate of sulphonation of the monosulphonic acids is greater than the rate of dissolution of the acenaphthene. The degree of 3-substitution in the monosulphonation of acenaphthene, p, was calculated

$$p = q \cdot r \qquad (1)$$

from equation (1), in which q is the degree of 8-substitution in the sulphonation of acenaphthene-3-sulphonic acid and r the initial content of the 3,8-disulphonic acid in the disulphonic acid mixture obtained from acenaphthene. Thus it was found that acenaphthene on treatment with 95·2% H_2SO_4 at 25° yields 68 ± 14% 3- and 32 ± 14% 5-sulphonic acid.

The relatively high degree of 3-substitution in the monosulphonation of acenaphthene is in line with the

[8] H. Cerfontain, A. Koeberg-Telder, C. Kruk, and C. Ris, *Analyt. Chem.*, 1974, **46**, 72.

significant amounts of 8-substitution in the sulphonation of the 3- and 5-sulphonic acids. This behaviour deviates from that observed in nitration [2e,9] and bromination [2b,c] where substitution adjacent to the ethylene bridge is substantially less.

The preferred 3-substitution in the sulphuric acid sulphonation of acenaphthene, as compared with the 2-substitution in naphthalene,[10] may be explained by an electrostatic, hyperconjugative, stabilizing proximity effect between the incoming sulpho-group and the adjacent methylene group and further by relatively reduced steric hindrance as compared with *e.g.* the 2-position in toluene, since C(2) in acenaphthene is bent away from C(3), the C(2)–C(2a)–C(3) angle being 132·8°.[11] A similar type of proximity effect has been proposed in the sulphonation of toluene to explain the lower enthalpy of activation for 2- compared with 4-substitution (for toluene in 95% H_2SO_4, *i.e.* with $H_2S_2O_7$ as sulphonating entity: f_2/f_4 (25°) = 0·58 ± 0·01; $\Delta H_2^{\ddagger} - \Delta H_4^{\ddagger} = -1{\cdot}3 \pm 0{\cdot}1$ kcal mol^{-1}; $\Delta S_2^{\ddagger} - \Delta S_4^{\ddagger} = -4{\cdot}9 \pm 0{\cdot}4$ cal mol^{-1} K^{-1} [12]).

Attempts to introduce a fourth sulpho-group into acenaphthene-3,5,8-trisulphonic acid failed, *e.g.* no reaction was observed on treatment of the trisulphonic acid with 115% H_2SO_4 at 25° for 2 days.

The absence of substitution *peri* to the sulpho-group at C(5) in *e.g.* acenaphthene-5-sulphonic acid and the 3,5,8-trisulphonic acid may be explained in terms of a prohibitively large steric hindrance for that substitution.

peri-Substitution has been observed in the bromination of 5-bromoacenaphthene,[2b] and in the nitration of 3,6-dinitro- and 3,5,8-trinitro-acenaphthene,[2e] and acenaphthene-5-sulphonic acid.[3] These phenomena illustrate again [13] that the steric requirements for sulphonation exceed those for nitration and bromination.

EXPERIMENTAL

Acenaphthene was Puriss grade (Rütgerswerke). Acenaphthene-3- and -5-sulphonic acid were prepared as described by Dziewonski and Stollyhwo [4] (for the structure assignment see ref. 5). Acenaphthene-3,5-disulphonic acid was obtained by hydrolysis of the corresponding bis(sulphonyl chloride); according to the n.m.r. spectrum it contained ⩽3% of the other isomers. The bis(sulphonyl chloride) was obtained as a precipitate on reaction of acenaphthene (0·1 mol) with a mixture of chlorosulphuric acid (0·45 mol) and carbon tetrachloride (80 ml) at 0—20° overnight and subsequent addition of ethanol (100 ml), m.p. 162—165°.

The sulphuric acid sulphonations were performed as described previously.[7a]

The ^{1}H n.m.r. spectra were obtained with a Varian HA 100 spectrometer, using for the sulphuric acid solutions pure tetramethylsilane (sealed capillary) or tetramethylsilane–carbon tetrachloride (1 : 1, v/v) as external references, and, for the D_2O solutions, sodium 2,2,3,3-tetradeuterio-5,5-dimethyl-4-silahexanoate as an internal reference. The chemical shifts in Table 1 were all converted to refer to the latter compound in D_2O as external reference.

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