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Sulfonation and sulfation in the reactions of the chloro- and dichlorophenols, 3-fluorophenol and (2,3-, 2,4- and 3,4-dichlorophenoxy)acetic acid with concentrated aqueous sulfuric acid and sulfur trioxide^{#,§,†}

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Abstract. The chloro- and dichlorophenols have been sulfonated with sulfuric acid and with SO_3 in aprotic solvents. In the sulfonations with concentrated aqueous sulfuric acid, the sulfonic acid isomer distribution is determined mainly by the *ortho-* and *para-*directing and activating effect of the hydroxy substituent; this is also the determining factor in the aprotic sulfonations using up to 1.0 equiv of SO_3 . Upon using larger amounts of SO_3 , the sulfonation isomer distribution is increasingly determined by additional sulfonation of the corresponding phenyl hydrogen sulfate, of which the -OSO₃H substituent is deactivating and mainly *para-* (and further *ortho-*) directing.

The sulfuric acid sulfonation of (2,3-,2,4- and 3,4- dichlorophenoxy)acetic acid leads to the exclusive formation of the 4-, 6- and 6-sulfonic acid, respectively.

Introduction

Despite the overwhelming number of reports on the biological activities, the environmental behaviour and the chemistry of the chlorophenols (CPs) and dichlorophenols (DCPs), the number of papers dealing with the electrophilic sulfonation of these aromatic compounds is almost negligible. Sulfonation of 2-CP with 87.0% H₂SO₄ was found to yield 80% of the 4-sulfonic acid and 20% of another product, which was tentatively assigned as the 6-sulfonic acid², while sulfonation of 4-CP yielded only the 2-sulfonic acid². The sulfuric acid sulfonation of 3-CP was earlier claimed to yield almost entirely the 6-sulfonic acid at both room temperature and at 100°C, while sulfonation with fuming sulfuric acid yielded the 4,6-disulfonic acid³. To our knowledge, no data are available on the sulfonation of DCPs other than our own report in which we showed that the sulfonation of 2,6-DCP in nitromethane yields the 4-sulphonic acid⁴. We now report on the sulfonation of all the CPs and DCPs with both concentrated aqueous sulfuric acid and sulfur trioxide, as well as on the sulfonation of 3-fluorophenol and (2.3-, 2,4- and 3,4-dichlorophenoxy)acetic acid (DCPA) with 98.5% H₂SO₄.

Results and discussion

The CPs and DCPs have been sulfonated with concentrated aqueous sulfuric acid at 20°C and with sulfur trioxide in

nitromethane at 0.0° C or in CCl₃F (freon 11) at 10.0° C. The structure of the sulfonation products and the composition of the reaction mixtures have been determined by ¹H NMR analysis⁵ and the various data are collected in the Tables I-IV. The ¹H NMR data of the sulfonic acids obtained in the reaction of 2,3-, 2,4- and 3,4-DCPA with 98.5% H₂SO₄ are given in Table V.

Table I ¹H NMR spectral data of the 3-fluorophenol- and chlorophenolsulfonic acids in 98.5% H_2SO_4 .

Phenol	δ (ppm) ^b						
substituents ^a	2-H	3-Н	4-H	5-H	6-H		
2-Cl-4-S	1	8.04	1	7.87	7.32		
-6-S		7.70-7.90	7.10-7.30	7.70-7.90	1		
-4,6-S ₂	1	8.22		8.30	1		
3-CI-4-S	7.23	ſ		8.04	7.10		
-6-S	7.18	1	7.20	7.77	}		
-4,6-S ₂	7.53			8.52			
3-F-4,6-S ₂	7.17			8.44			
4-Cl-2-S°		7.77		7.54	7.09		
$-2,6-S_2^{c}$	1	8.08	1	8.08			
2,3-Cl ₂ -4-S		ĺ	1	7.70	7.17		
-Cl ₂ -6-S		7.26	7.90				
2,4-Cl ₂ -6-S		7.71		7.77			
1-SO-2,4-Cl2-5-Sd	1	7.90		}	8.19		
1-SO-2,4-Cl2-6-S		7.95		8.00	1		
2,5-Cl ₂ -4-S		8.07			7.30		
2,6-Cl ₂ -4-S		7.94		7.94			
3,4-Cl ₂ -6-S	7.23			7.84	1		
3,5-Cl ₂ -2-S			7.22	1	7.06		
		1		1	1		

^a S stands for SO₃H. ^b The *ortho* and *meta* J_{HH} s were found to be 9–10 and ≈ 1.5 Hz, respectively. ^{c,d} Solvents 92.2 and 105.1% H₂SO₄, respectively.

[#] Dedicated to Prof. Dr. G. J. M. van der Kerk on the occasion of his 75th birthday.

[§] Aromatic sulfonation. Part 100. For part 99, see ref. 1.

[†] For reasons of convenience, the aromatic ring positions of the sulfonic acids and hydrogen sulfates have been numbered as for the parent substrate.

Phenol H_2SO_4 substituents(wt $\%$, $\pm .2$)	H₂SO₄	Reaction	Phenolsulfonic acid product distribution $(\%, \pm 2)^a$					
	$(wt \%, \pm .2)$	time (ks)	2-8	4-S	5-S	6-S	4,6-S ₂	
2-Cl	98.5	3.6 9.9 18 86		79 77 76 72		17 14 11 8	4 8 12 20	
3-Cl	98.5	2.4 4.2 8.7 19 83		44 40 31 20 5		44 40 31 20 5	12 20 38 60 90	
3-F	98.5	0.30		42 ^b		58 ⁶		
4-Cl	92.9	66	> 98					
2,3-Cl ₂	92.9 96.9 98.5	19 12 10		48 44 42		52 56 58		
2,4-Cl ₂	98.5 105.1	158			59	100 41		
2,5-Cl ₂ 2,6-Cl ₂	98.5	1.5		100 100				
3,4-Cl ₂ 3,5-Cl ₂	98.5 98.5	1.8 3.0	100			100		

Table II Sulfonic acid product distribution in the reactions of chlorophenols with sulfuric acid at 20°C.

^a S stands for SO₃H. ^b Determined from the isolated potassium sulfonate mixture.

Table III ¹H NMR spectral data of the chlorophenolsulfonic acids in ${}^{2}H_{2}O$.

Phenol	δ (ppm)						
substituents ^a	2-H	3-H	4-H	5-H	6-H		
2-Cl-4-S		7.84		7.63	7.11		
-4,6-S ₂		7.97		8.69			
-3-Cl-4-S	7.03			7.82	6.83		
-6-S	7.04		6.97	7.62			
-4,6-S ₂	7.13			8.50			
3-F-4-S				7.58	6.58		
-6-S				7.76			
1-SO-4-Cl ^b	7.48	7.29		7.29	7.48		
1-SO-4-Cl-2-S ^b		7.88		7.58	7.66		
4-Cl-2-S		7.64		7.32	6.84		
-3-\$	7.21		ļ	7.28	6.76		
2,3-Cl ₂ -4-S				7.52	6.65		
2,3-Cl ₂ -6-S			6.80	7.29			
2,4-Cl ₂ -5-S		7.57			7.44		
2,5-Cl ₂ -4-S		8.05			7.27		
1-SO-2,6-Cl ₂ ^c			- 7. 2-7 .6 -	<u> </u>			
2,6-Cl ₂ -4-S ^c				7.98			
1-SO-3,4-Cl ₂	7.90			7.69	7.95		
1-SO-3,4-Cl ₂ -6-S	8.31			8.43			
3,4-Cl ₂ -6-S	7.57			8.22			
3,5-Cl ₂ -4-S	7.50				7.50		

^a S stands for SO₃⁻. ^b (Di)potassium salt; $pH \approx 7$. ^c Solvent (²H₃)nitromethane; see ref. 5.

Sulfonation in sulfuric acid

2-CP with 98.5% H_2SO_4 (see Table II) yields the 4- and 6-sulfonic acids with an initial isomer ratio of 80/20 and 4-CP, with 92.9% H_2SO_4 (as reported previously for a lower sulfuric acid concentration²), yields only the 2-sulfonic acid. 3-CP in 98.5% H_2SO_4 yields the 4- and 6-sulfonic acids (in a ratio of 50/50) both of which slowly yield the 4,6-disulfonic acid, each with an apparent first order rate coefficient of 0.053 \pm 0.002 ks⁻¹. Fluorophenol yields the 4- and 6-sulfonic acids in a ratio of 42/58. The con-

version of the mixture of these monosulfonic acids into the 4.6-disulfonic acid was found to be strictly of the first order over a period of time of three half lives with a rate coefficient of 0.20 ± 0.01 ks⁻¹, which is thus the rate coefficient of the conversion of both the 4- and the 6-sulfonic acid. The observed f_4/f_6 substitution ratio for 3-fluoroand 3-chlorophenol deviates strongly from the value of 0.009, predicted for both substrates on the basis of the principle of additivity of substituent effects, as obtained by f_4/f_6 = $({}^{\text{HO}}f_4/{}^{\text{HO}}f_2) \cdot ({}^{\text{Hig}}f_2/{}^{\text{Hig}}f_4)$, using the reported f_2/f_4 ratios for the sulfuric acid sulfonation of PhOH², PhF, PhCl and PhMe⁶ (vide infra) by $H_2S_2O_7$ as sulforating entity. A similar deviation - but somewhat less pronounced - was observed for 3-fluoro- and 3-chlorotoluene, the observed⁷ versus the predicted f_4/f_6 ratios being 0.11 versus 0.009 and 0.20 versus 0.010, respectively. The sulfonation of 2,3-DCP yields both the 4- and the 6-sulfonic acid. The ¹H NMR spectra showed two AB patterns with the low-field signals at 7.90 and 7.70 ppm, while the high-field signals at 7.26 and 7.19 ppm are partly overlapping. By comparison with the ¹H NMR data of the 2,3-DCP-4-sulfonic acid, formed on reaction of 2,3-dichloroanisole in 98.5% H₂SO₄ as a result of sulfonation and subsequent demethylation⁸, the signals of 7.70 and 7.19 ppm have been assigned to the 5- and 6-H of 2,3-dichlorophenol-4-sulfonic acid. On increasing the sulfuric acid concentration from 92.9 to 98.5% H₂SO₄, the 4- to 6-sulfonic acid ratio decreases from 0.92 to 0.72, which is attributed to a gradual change-over in the mechanism of sulfonation, the effective sulfonating entity at low and high sulfuric acid concentrations being $H_3SO_4^+$ and $H_2S_2O_7$, respectively⁶.

The sulfonation of 2,4-DCP with 98.5% H_2SO_4 yields exclusively the 6-sulfonic acid. However, on using 105.1% H_2SO_4 , the 5- and 6-sulfonic acids are formed in a 3/2 ratio. This may be explained by presuming that the 2,4-DCP in 105.1% H_2SO_4 will be present to a very significant degree as its phenyl hydrogen sulfate (this infers, as observed previously⁴, that the sulfation is much more rapid than the sulfonation) which will then be in effect the substrate species undergoing the ring sulfonation. In electrophilic aromatic substitution, the OSO₃H substituent is *pa*-

Phenol Reagent ^a	enol Reagent ^a Equiv ituents SO ₃	Equiv of	Phenolsulfonic acid product distribution $(\%, \pm 2)^{b}$						
		2-S	3-S	4-S	5-S	6-S	4,6-S ₂		
2-Cl	N	1.0 3.0			100 97			3	
3-Cl	N	1.0 2.0 4.0 6.0			- 74 74 74		26 26 22	4	
4-Cl	F	1.0° 2.0 ^d 3.0° 4.0	- 99 84 45 47	<2 16 55 53					
2,3-Cl ₂	F	1.0			44		56 25		
2,4-Cl ₂ 2,5-Cl ₂	F N	5.0 4.0			100	100			
2,6-Cl ₂ 3,4-Cl ₂ 3,5-Cl ₂	N F F	1.1 ^r 5.0 ^g 2.0 ^h			100		100		

Table IV S	Sulfonation of t	he chloro- and	dichlorophenols wi	ith SO ₃ in	nitromethane	and	CCl_3F .
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^a N stands for nitromethane and F for CCl₃F; for N and F, the reaction conditions were 4 h at 0.0° C and 30 min at 10.0° C, respectively. ^b S stands for SO₃⁻. ^c The spectrum showed the presence of 59% of the substrate and 41% of its potassium sulfate. ^d The spectrum recorded after neutralization and freeze drying showed the presence of 31% of potassium 2-sulfo-4-CP sulfate, together with 6% of the starting material and 63% of the potassium 4-CP sulfate. ^c The spectrum showed the presence of 11% of the starting material, 74% of 4-CP-2- and 14% of 4-CP-3-sulfonic acid. ^f Solvent (²H₃) nitromethane; see ref. 5. ^g The spectrum showed the presence of 26% of 3,4-DCP-6-sulfonic acid, 14% of 6-sulfo-3,4-DCP hydrogen sulfate, 19% of the starting material and 41% of 3,4-DCP hydrogen sulfate. ^h The spectrum showed the presence of 9% of the starting material and 91% of 3,5-DCP-4-sulfonic acid.

Table V ¹H NMR spectral data of the sulfonic acids of (2.3-, 2.4and 3.4-dichlorophenoxy)acetic acid (DCPA-S) in 98.5% $H_2 SO_4^{a}$.

Sulfonic acid	δ (ppm)					
	CH ₂	2-H	3-H	5-H	6-H	
2,3-DCPA-4-S 2,4-DCPA-6-S 3,4-DCPA-6-S	5.23 5.11 5.25	7.36	7.67	8.23 7.74 8.01	7.28	

^a S stands for SO₃H.

ra + ortho directing and (contrary to the OH) deactivating. The 2-Cl is directing the sulfonation of 2,4-dichlorophenyl hydrogen sulfate towards the 5-position and its 1-OSO₃H to the 6-position. However, because of steric hindrance with the 2-Cl, the SO₃H group of the 1-OSO₃H substituent will be directed away from the 2-Cl and towards 6-H because of enhanced stabilization due to coplanarity. The steric hindrance encountered in sulfonating the 6-position will thus be greater for 2,4-dichlorophenyl hydrogen sulfate than for 2,4-DCP. In fact, in 105.1% H₂SO₄, the 5-substitution predominates over the 6-substitution. As expected on the basis of the results obtained with 2-, 3- and 4-CP (vide supra), 2,5- and 2,6-DCP in 98.5% H₂SO₄ both yield only the 4-sulfonic acid and 3,4-DCP only the 6-sulfonic acid. Under these conditions, 3,5-DCP gives exclusively the 2-sulfonic acid; this is mainly caused by the strongly deactivating effect of the two chlorines for the substitution at C(4), the ${}^{Cl}f_2/{}^{Cl}f_4$ ratio being only 0.004⁶.

Sulfonation with SO_3 in nitromethane and trichlorofluoromethane

Upon treatment of the CPs and DCPs with SO_3 in nitromethane at 0.0°C, sulfonation occurred only with 2-CP, 3-CP and 2,5-DCP. The other chlorophenols were therefore sulfonated with the far more reactive SO_3 in CCl_3F reagent system.

On sulfonation of an hydroxyarene (ArHOH) with SO₃ in aprotic solvents, the initial reaction involves the rapid formation of the aryl hydrogen sulfate (step 1)^{4.9}. The sulfonic acid products may then be formed via two routes: first, by regeneration of the hydroxyarene and SO₃ and subsequent ring sulfonation (steps -1 and 2), and second, by ring sulfonation of the aryl hydrogen sulfate (step 3), which will be very much slower than step 2 and which may lead to a different substitution pattern of the aryl group than that found in step 2. This is then followed by *O*-desulfonation (step 4). The first route is mainly operative on using a deficient amount SO₃, while the second route becomes more important on using an excess of SO₃⁴.

ArHOH	$+ SO_3$	=	ArHOSO ₃ H	(1	I)
				· · ·	

ArOH + SO₃ \rightarrow HO₃SArOH (2)

$$ArHOSO_{3}H + SO_{3} \rightarrow HO_{3}SAr'OSO_{3}H$$
 (3)

$$HO_3SAr'OSO_3H \Rightarrow HO_3SAr'OH + SO_3$$
 (4)

The sulfonation of 2-CP with 1.0 equiv of SO₃ in nitromethane (see Table IV) yielded exclusively the 4-sulfonic acid, as expected on the basis of the σ_p^+ values of the hydroxy and chloro substituents¹⁰. Sulfonation with 3.0 equiv of SO₃ also led to the formation of the 4-sulfonic acid¹¹, in addition to some 4,6-disulfonic acid. The formation of the 4-sulfonic acid in the reaction with 3.0 equiv of SO₃ does not exclude the route via the phenyl hydrogen sulfate of 2-CP, since sulfonation of 2-chlorophenyl methanesulfonate, which is an ester analogue of the presumed 2-chlorophenyl hydrogen sulfate, also yields the 4-sulfonic acid¹².

Reaction of 3-CP with 1.0 equiv of SO_3 in nitromethane does not yield any sulfonic acid; reaction with 2.0 and

4.0 equiv of SO₃ resulted in the formation of 74% 4- and 26% 6-sulfonic acid, whereas reaction with 6.0 equiv of SO₃ led to additional sulfonation of the 6-sulfonic acid yielding the 4,6-disulfonic acid. The constancy of the monosulfonic acid isomer ratio and the absence of sulfonic acid formation using 1.0 equiv of SO₃ indicate the inertness of 3-chlorophenyl hydrogen sulfate towards isomerization via O-desulfonation and C-sulfonation. The ring sulfonation, using ≥ 2.0 equiv of SO₃, will thus occur by sulfonation of the hydrogen sulfate.

Sulfonation of 4-CP with 1.0 equiv of SO₃ in CCl₃F, followed by aqueous work-up of the reaction mixture, resulted in the presence of 59% of the substrate and 41% of its potassium sulfate. Reaction with 2.0 equiv of SO₃ yielded exclusively the 2-sulfonic acid as the ring substituted product, whereas with 4.0 and 5.0 equiv of SO₃, the sulfonation at the 3-position becomes competitive. The increase in the amount of 3-sulfonic acid at the expense of the 2-isomer is again taken to illustrate additional sulfonation via the hydrogen sulfate. Apparently, the partial rate factor is even smaller for substitution *ortho* to OSO₃H than *ortho* to Cl.

The change-over in the substrate species being sulfonated is also apparent with 2,3-DCP. On reaction with 1.0 equiv of SO_3 , the 4- to 6-sulfonic acid ratio of 0.79 is comparable in magnitude with that of the sulfuric acid sulfonation (see Table II), while on reaction with 4.0 equiv of SO_3 it is substantially greater, *viz.* 3.0.

The sulfonation of 2,4- and 3,5-DCP with an excess of SO₃ is also likely to proceed via the respective hydrogen sulfate, as 2,4-DCP with 5.0 equiv of SO_3 yields the 5-sulfonic acid and 3,5-DCP with 2.0 equiv of SO₃ the 4-sulfonic acid as the exclusive products, whereas the concentrated aqueous sulfuric acid sulfonations, which proceed via the unprotonated and unsulfated phenols (vide supra), yield exclusively the 6- and 2-sulfonic acid, respectively. For 2,5-, 2.6and 3,4-DCP, the ring substitution pattern is similar for the sulfonation with SO_3 in aprotic solvents as with 98.5%H₂SO₄ (cf. Tables IV and II, respectively) and no conclusions as to the intermediacy of the hydrogen sulfates can be drawn. However, the sulfonation of 3,4-DCP with 5.0 equiv of SO₃ in CCl₃F resulted in the formation of only 26% 6-sulfonic acid, the other components, after aqueous work-up of the reaction mixture, being 3,4-DCP and its potassium sulfate. The low degree of ring sulfonation in CCl₃F, despite the five-fold excess of SO₃, strongly indicates the very predominant presence of the hydrogen sulfate of 3,4-DCP, which is quite unreactive towards sulfonation, as was observed with 4-CP.

Sulfonation of 2,3-, 2,4- and 3,4-DCPA in 98.5% H₂SO₄

The reaction of (2,3-dichlorophenoxy)acetic acid (2,3--DCPA) in 98.5% H_2SO_4 at 20°C was completed within 30 min yielding only the 4-sulfonic acid, which started to precipitate after 45 min. The absence of the 6-sulfonic acid – which is the additional sulfo product with 2,3-DCP – is due to the steric repulsion between the 1-OCH₂CO₂H and the 2-Cl as result of which the CH₂CO₂H moiety is directed to the 6-H and blocks the sulfonation at C(6). 2,4- and 3,4-DCPA both yield the 6-sulfonic acid by apparent firstorder kinetics, the respective rate coefficients being $(3.0 \pm 0.1) \cdot 10^{-4}$ and 0.26 ± 0.01 ks. The very much lower reactivity of 2,4- as compared with 3,4-DCPA is due to the 2-chloro substituent which forces the CH₂CO₂H moiety to point to 6-H, thus strongly enhancing the steric hindrance for substitution at the 6-position.

Experimental

The substrates were obtained commercially except for 2,3- and 3,5-DCP, which were synthetized from the corresponding anisoles

by reaction with hydrogen iodide¹³. The sulfonation with sulfuric acid was carried out at 20°C by dissolving 0.5 mmol of the phenol in 1.0 ml sulfuric acid of the desired strength. The reaction mixtures as such were then subjected to 'H NMR analysis after appropriate time intervals. The sulfonations with SO3 in nitromethane at 0.0°C were performed and worked up to obtain the potassium sulfonates as previously described⁴. For the sulfonations with SO₃ in CCl₃F, 1.0 mmol of the phenol was dissolved in 7.0 ml of CCl₄F at 10.0°C. Under a flow of dry nitrogen, 7.0 ml of a solution of the desired amount of SO3 in CCl3F, also at 10.0°C, was added, resulting in the formation of an oil-like precipitate. After 30 min, 1.0-2.0 ml of ${}^{2}H_{2}O$ was added and the resulting solution stirred vigorously until the precipitate had dissolved. The solvent layers were then separated. From the aqueous solution the residual CCl₃F was removed by bubbling dry nitrogen through the solution for 30 min and an 'H NMR spectrum was then recorded. The aqueous solution was subsequently neutralized with 10% aqueous KOH and subjected to freeze drying. In some cases, an ¹H NMR spectrum of the potassium sulf(on)ate residue in ²H₂O was recorded.

The structural assignments of the products were obtained from the ¹H NMR spectra of the sulfuric acid reaction mixture solutions and from the isolated sulfonic acids or potassium sulfonates, in ²H₂O as solvent, on the basis of the observed chemical shifts, absorption-area ratios and coupling constants in combination with the known shielding parameters for the OH, Cl, SO₃H and OSO₃H substituents^{4,5,14}. The compositions of the reaction mixtures were determined by multicomponent ¹H NMR analysis⁵. The ¹H NMR spectra were recorded using Varian XL-100 12 FT, Bruker WM 250 and AC 200 spectrometers; the chemical shifts are relative to virtual internal TMS.

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