AROMATIC SULFONATION – XLII^a

SULFONATION OF NEOPENTYLBENZENE AND 1,3,5-TRINEOPENTYLBENZENE-STERIC INTERACTION BETWEEN A NEOPENTYL AND SULFO FUNCTION IN THE ORTHO-POSITION^b

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Abstract—The partial rate factors for the sulfonation of neopentylbenzene in 89.9% H₂SO₄ at 25.0° were determined to be $f_p = 82 \pm 12$, $f_m = 5.7 \pm 1.4$ and $f_a = 1.2 \pm 0.6$ The low f_a/f_p ratio is ascribed to steric hindrance for *ortho*-substitution. Evidence for the non-bonded interaction of a neopentyl and sulfo substituent in ortho-position was also obtained from a dynamic NMR study of 1,3,5-trineopentyl-2-benzenesulfonyl chloride.

Recently we have reported the isomer distribution in the sulfonation of phenylmethanesulfonic acid with sulfuric acid.¹ The low degree of *ortho*-substitution can be explained in terms of both steric and electronic effects of the $-CH_2SO_3H$ substituent. In order to possibly differentiate between these effects it was desired to sulfonate a model compound of which the substituent would exhibit similar steric requirements, but an opposite electronic effect. Neopentylbenzene meets these requirements, since the size of the neopentyl and methylsulfonic acid group is about the same, and the former group has an activating, but the latter one a deactivating effect on electrophilic ring substitution (for sulfonation ${}^{-CH_8SO_3H}f_p = (4.6 \pm 1.0)$

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^bTaken in part from the thesis of C. Ris (1973).

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[†]The partial rate factors of the $-CH_2SO_3H$ substituent for *meta*- and *para*-substitution are $10 \times$ smaller than was reported erroneously.¹

 \pm Under the present conditions, isomerization of the sulfonic acid products can be excluded (cf Ref 3).

 $\times 10^{-4}$ ¹).[†] The sulfonation of neopentylbenzene was therefore studied in some detail. In order to gain further information on the steric interference of a neighbouring neopentyl and sulfo group, a dynamic NMR study was made on the sulfonation product of 1,3,5-trineopentylbenzene.

Bygdén has reported that sulfonation of neopentylbenzene with fuming sulfuric acid yields mainly the 4-sulfonic acid.²

RESULTS AND DISCUSSION

Neopentylbenzene (NPB). Varying amounts of NPB (1.5-5 wt. %) were sulfonated at 25° with sulfuric acid.‡ with an increasing amount of sulfonated substrate, the degree of *meta*-substitution decreases, that of *para*-substitution increases, and that of *ortho*-substitution remains constant. The isomer distributions under conditions of homogeneous sulfonation were obtained by graphical extrapolation to zero substrate conversion. The results are in Table 1. The rate of sulfonation of neopentylbenzene in sulfuric acid was also determined. The pseudo first order rate constants are in Table 2.

% H2SO4 (±0·1)	Temp ℃	Isomer distribution, %				
		ortho (±1·0)	meta (±2)	para (±3)	f_o/f_p	f_m/f_p
89.9	25	2.5	12	86	0.015 ± 0.006	0.070 ± 0.014
95.4	25	3.8	14	82	0.023 ± 0.006	0.085 ± 0.018
94.9	80	3.8	-			
98·5	25	3.1	13	84	0.019 ± 0.007	0.078 ± 0.018

Table 1. Sulfonation of neopentylbenzene

% H₂SO₄ (±0·1)	$ps^{k_1 \cdot 10^4}, sec^{-1}$ (±10%)	ps ^k '' ^k benzene (±2)
84 ·7	9.9	
85.6	12.1	
87-4	34-2	
88·2	53	
88.9	77	16.6*
90.0	134	15-2*

 Table 2. Sulfonation of neopentylbenzene at 25.0°

*Determined graphically from graphs of log k against % H₂SO₄ for NPB and benzene.⁴

The partial rate factors for sulfonation in 89.9% H_2SO_4 at 25° were calculated from the reactivity of NPB relative to benzene,⁴ viz (16±2):1, and the isomer distribution to be $f_p = 82 \pm 12$, $f_m = 5.7 \pm 1.4$ and $f_o = 1.2 \pm 0.6$. The reactivities of the para-positions of NPB and toluene⁵ are the same. Accordingly, the sulfonation of NPB in 89.9% H_2SO_4 will be effected by the same sulfonating entity which effects the sulfonation of toluene in 89.9% H_2SO_4 , viz $H_2S_2O_7$. The neopentyl partial rate factors thus refer to the $H_2S_2O_7$ sulfonation mechanism.⁶

Sulfonation of the ortho-position in toluene by the $H_2S_2O_7$ mechanism encounters substantial steric hindrance $(\Delta S_p^* - \Delta S_o^* = 4.9 \pm 0.4 \text{ eu}^6)$. The much lower value of $n^{-Pe}f_o$ compared with ${}^{Me}f_o$ may therefore be explained in terms of a large degree of steric hindrance for sulfonation ortho to the neopentyl substituent. The independence of the low degree of ortho-substitution with variation in temperature (Table 1) is in line with this explanation. The f_o/f_p ratio of NPB decreases in the sequence nitration⁷ > chlorination⁷ > bromination⁷ > acylation⁷ > sulfonation. This order bears out Ingold's prediction concerning the steric requirements of these substitution reactions.⁸

The f_m/f_p ratio of NPB is in between that of toluene⁶ and that of t-butylbenzene.⁹ This may be explained in terms of hyperconjugative electron release for *para*- and not for *meta*-substitution. This electron release apparently decreases in the order Me > *n*-Pe > *t*-Bu, which indicates that

C-H hyperconjugation is more effective than C-C hyperconjugation.

Sulfonation of p-NPB-sulfonic acid with 107% H_2SO_4 yields exclusively 2,4-NPB-disulfonic acid.

1,3,5-Trineopentylbenzene (TNPB). Sulfonation of TNPB with chlorosulfuric acid in chloroform as a solvent at 0° yields solely the mono-sulfonyl chloride. Treatment with an excess of this reagent at 60° does not lead to further sulfonation, but to decomposition.

Dynamic NMR spectroscopy. A low temperature NMR study was made of the 2-TNPB-sulfonyl chloride in CCl₃F. Characteristic spectra with the assignments are shown in Fig 1. The spectra may be explained in terms of restricted rotation of the two neopentyl groups *ortho* to the sulfonyl chloride group over an angle of $\sim 180^\circ$. Recent studies on neopentylbenzene indicate a strong preference for the two conformations in which the quaternary C atom of the neopentyl group is located above or below the plane of the benzene ring.¹⁰ Accordingly, the preferred conformations of 2-TNPB-sulfonyl chloride are 1 and 2. The interconversion of 1 and 2 will proceed via 3, and not via 4, which has a much higher energy content. At low temperatures two doublets are observed for the two methylene hydrogens which are diastereotopic.¹¹ Apparently, the rotation on the Carom-Cbenzylic bond is slow on the NMR time scale because of non-bonded repulsive interaction between the methylene hydrogens and the sulfonyl chloride group in conformation 3.

The significant downfield shift of methylene hydrogen adjacent to the $-SO_2Cl$ group is ascribed to field and anisotropy effects, and is not the result of an inductive effect, for the chemical shift of the other methylene hydrogen is about equal to that of methylene signal of the neopentyl group *para* to the $-SO_2Cl$ group.

At relatively high temperatures the rotation on the $C_{arom}-C_{benzyllc}$ bond is rapid on the NMR time scale, the two methylene hydrogens are equivalent, and a singlet absorption for the methylene hydrogens is observed. The coalescence temperature is $-62 \pm 3^{\circ}$.

This is the first example of restricted rotation of a monosubstituted TNPB derivative. Restricted





Fig 1. Temperature dependence of NMR methylene absorptions of 2-TNPB-sulfonyl chloride in CCl₃F.

rotation of (a) neopentyl group(s) has been demonstrated by dynamic NMR studies of 2,4-dihalogeno-1,3,5-trineopentylbenzenes^{12, 13} and 2,6-disubstituted neopentylbenzenes¹⁴ and 1,2,3,4-tetramethyl-5,6-dineopentylbenzene.¹⁵

The steric intererence between neighbouring neopentyl and sulfo groups will be smaller in o-NPB-sulfonic acid than in 2-TNPB-sulfonic acid, becuase of buttressing of the sulfonic acid group by the other ortho-neopentyl group in 2-TNPBsulfonic acid.

EXPERIMENTAL

Materials. Neopentylbenzene was prepared as described¹⁶ and purified by GLC (column 6 m $\times \frac{3}{8}$ in, 15% carbowax 20 m, 120°). 1,3,5-Trineopentylbenzene was obtained from Dr. P. Martinson.¹⁷ Sodium *p*-NPB-sulfonate was prepared by sulfonation of NPB.² 2-TNPBsulfonyl chloride was prepared from TNPB according to a standard procedure,¹⁸ m.p. 82-84°, mass spectrum (AE1 MS-9, 70 eV) parent peak m/e = 386 (2.07%), isotope peak m/e = 388 (0.94%), base peak (= 100%) m/e = 57. The NMR spectrum (CCl₄, 30°) exhibits singlet absorptions at δ (ppm) = 6.97 (2 H), 3.21 (4 H), 2.49 (2 H), 0.97 (9 H) and 0.95 (18 H); IR (SO₂ group): 1370, 1360, 1170, 1160 cm⁻¹ (cf Ref 19). Potassium 2-TNPB-sulfonate was obtained from the sulfonyl chloride by treatment with an ethanolic KOH aq soln. The NMR spectrum (CD₃OD, 30°) exhibits singlet absorptions at δ (ppm) = 6.92 (2 H), 3.33 (4 H), 2.46 (2 H), 0.95 (27 H). IR ($-SO_3^-$ group): 1240–1150, 1175, 1010, 690 cm⁻¹ (cf Ref 20).

Spectrometers. A Zeiss PMQ-2 UV spectrometer and a Varian HA 100 NMR spectrometer, equipped with a Time Averaging Computer, were used.

Procedures. The monosulfonation of NPB was performed as described before.²¹ Rate measurements were made by UV in cuvettes with a pathlength of 20 and 50 mm at $\lambda = 235$ nm.²²

Product and isomer analysis. The NMR spectra of the monosulfonation mixture of NPB in sulfuric acid exhibit two methylene hydrogen singlet absorptions at 2.70 and

3.09 ppm. On the basis of a comparison with the three isomeric toluenesulfonic acids⁵ these two peaks were assigned to (p - + m) and to o-NPB-sulfonic acid respectively. The ratio o/(p + m) was determined from the ratio of the two methylene peaks.

The NMR spectrum of *p*-NPB-sulfonic acid in 107% H_2SO_4 after 1 hr at 25° exhibits solely an aromatic ABX pattern ($\delta_A = 8.05$, $\delta_B = 8.40$, $\delta_x = 8.82$ ppm; $J_{AB} = 8.7$, $J_{BX} = 1.2$ Hz) and a Me absorption at $\delta = 3.30$ ppm which were assigned to 2,4-NPB-disulfonic acid.

The degree of *meta*-substitution of NPB was determined from the NMR spectrum of the disulfonic acid mixture which results upon addition of an amount of 115% H₂SO₄, sufficient to yield a solution of an acid strength of 107% H₂SO₄. The spectrum illustrates the presence of mainly 2,4-NPB-disulfonic acid (see just before). In addition it contains an aromatic A₂X pattern ($\delta_A = 8.30$, $\delta_X = 8.59$ ppm, $J_{AX} = 1.0$ Hz) and a Me signal at $\delta = 2.96$ ppm of low intensity which were assigned to 3,5-NPB-disfulfonic acid and a tiny absorption at 8.18 ppm, possibly due to a small amount of 3,4-NPB-disulfonic anhydride,²³ the methyl absorption of which will coincide with the Me signal of the 3,5-disulfonic acid at $\delta = 2.96$ ppm.

The degree of *meta*-substitution in the sulfonation of NPB is thus equal to the ratio of the methyl absorptions at $\delta = 2.96$ and 3.30 ppm and was calculated accordingly.

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