Substituent Effects in Five-membered Rings: σ_{Het} Constants for Thia- and Oxa-Substituents from the Reaction of Arenesulphonyl Chlorides with Aniline

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σ_{Het} Values for thia- and oxa-substituents in five-membered heterocycles are derived from the rate constants for the reactions of sulphonyl chlorides with aniline in methanol. These values, which are negative and similar to σ^+, are in agreement with the S_AN mechanism previously proposed.

THE kinetics of reaction of some ' aromatic ' sulphonyl chlorides with anilines in methanol have been widely investigated[1] and an S_AN mechanism involving the formation of an intermediate complex has been proposed.[2] Hammett treatment of the data gives information on the effects of the heteroatom and of the substituent on the side chain reactivity in this reaction. By

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[1] (*a*) O. Rogne, *J. Chem. Soc.* (*B*), 1971, 1855; A. Arcoria, E. Maccarone, G. Musumarra, and G. A. Tomaselli, *J. Org. Chem.*, (*b*) 1973, **38**, 2457; (*c*) 1974, **39**, 1689; (*d*) p. 3595; (*e*) E. Maccarone, G. Musumarra, and G. A. Tomaselli, *Ann. Chim.* (*Italy*), 1973, **63**, 861.

[2] (*a*) E. Ciuffarin, L. Senatore, and M. Isola, *J.C.S. Perkin II*, 1972, 468; (*b*) E. Maccarone, G. Musumarra, and G. A. Tomaselli, *J. Org. Chem.*, 1974, **39**, 3286.

regarding the heteroatoms as substituents,[3] the σ_{Het} constants for the replacement of a CH=CH in the benzene ring by an oxygen (oxa-substituent) or a sulphur atom (thia-substituent) can be obtained from equation (1) where

$$\log k = \rho\, \sigma_{Het} + \log k_0 \qquad (1)$$

ρ (1.02) and $\log k_0$ (−1.168) are respectively the slope and the intercept of the Hammett plot * for the reaction where ρ (1.02) and $\log k_0$ (−1.168) are respectively the slope and the intercept of the Hammett plot * for the reaction of substituted benzenesulphonyl chlorides with aniline in methanol.[1] σ_{Het} Values are reported in the Table together with σ and some σ^+ values from the literature. The differences in the latter values can be ascribed mainly to experimental error, but it has also been claimed that σ^+ varies with the reaction considered, depending on the electron demand,[12] although the application of the extended selectivity principle to such 'substituents' suggests this is not so.[13]

Substituent constants for the heteroatoms in five-membered rings

	σ [a]	σ^+ [b]	σ^+ [c]	σ^+ [d]	σ^+ [e]	σ^+ [f]	σ^+ [g]	σ_{Het} [h]
α-O	1.04	−0.94	−1.26	−0.89	−0.91	−0.93	−0.85	−1.03
β-O	0.25	−0.49	−0.76	−0.42	−0.45	−0.44	−0.44	−0.88
α-S	0.67	−0.84	−1.13	−0.79	−0.79	−0.79	−0.76	−1.06
β-S	0.11	−0.47		−0.38	−0.43	−0.52	−0.44	−0.50

[a] From the pK_a of unsubstituted carboxylic acids;[4] pK_0 = 4.20. Other σ values calculated from the hydrolysis of carboxylic esters [5] and the solvolytic rearrangement of β-arylethyl tosylates by the Yukawa–Tsuno equation [6] are very close to zero, apart from $\sigma_{\alpha\text{-}O}$ which is *ca.* 0.33. [b] From solvolysis of 1-arylethyl acetates.[7] [c] From protiodemercuriation.[8] [d] From pyrolysis of 1-arylethyl acetates.[9] [e] From protiodesilylation.[10] [f] From electrophilic reactivity using the 'extended selectivity treatment.'[11] [g] From the solvolysis of alkyl chlorides.[5] [h] This work.

σ_{Het} Constants follow the sequence of σ^+, apart from $\sigma_{\beta\text{-}O}$ which discrepancy, however, is not surprising, taking into account the inaccuracies in its derivation from equation (1).†

To check the reliability of σ_{Het} values, the logarithms of the rate constants of reaction of benzene-, furan-, and thiophen-sulphonyl chlorides with aniline in acetonitrile [15] have been plotted against σ_{Het} constants, a very good Hammett plot being obtained (ρ 1.00; $r = 0.997$). This confirms that for the reaction with aniline σ_{Het} constants are negative and different from σ given by the pK_a of carboxylic acids.[4]

For the reaction between substituted thiophen-2-sulphonyl chlorides ($XC_4H_3S{\cdot}SO_2Cl$) and aniline in methanol,[1e] which can be regarded as disubstituted benzene derivatives, we can recalculate $\sigma_{\alpha\text{-}S}$ from equation (2), assuming the constancy of ρ and the additivity of

$$\log k = \rho\,(\sigma_X + \sigma_{\alpha\text{-}S}) + \log k_0 \qquad (2)$$

substituent effects.[16] σ_X Is the σ constant for the X substituent in the thiophen ring (σ_m and σ_p for the 4- and 5-positions respectively), while ρ and $\log k_0$ have the same values as those used in equation (1).

In the absence of interactions between the thia and X substituents, $\sigma_{\alpha\text{-}S}$ should be constant and equal, within experimental error, to the value calculated for the unsubstituted sulphonyl chloride. For some 5-substituted derivatives (CH_3, Cl, Br, I), in fact, an average value $\bar{\sigma}_{\alpha\text{-}S} = -0.98 \pm 0.06$ is found, indicating that the additivity principle is followed.

For nitrothiophen-2-sulphonyl chlorides, instead, different $\sigma_{\alpha\text{-}S}$ values are found [−0.51 and −0.39 (−0.86, using the σ^- value for the nitro-substituent) respectively for the 4- and 5-derivatives] showing deviation from additivity. The lower conjugation between the thia-substituent and the reacting side chain, can be ascribed, in this case, to direct electronic interaction between the thia- and nitro-substituents.

Although limitations due to the magnitude of experimental errors do not allow fine distinctions, the following general conclusions can be drawn from the above results: σ_{Het} values, which have been calculated by a Hammett-like treatment, are always negative and their values similar to σ^+ indicating that the electron-donating character of the heteroatoms in the ground state is different from that in the transition state; in particular, with ρ positive, conjugation is less important in the

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* For all substituents except *p*-OCH_3.

† The value −0.88 was calculated by us from a single rate constant and not from a set of data; the value −0.49 [7] was extrapolated from rate constants measured in the range 60—85 °C; the accuracy (±0.021) in −0.415 [9] was obtained by applying 50% confidence limits in statistical analysis; the value −0.44,[11c] which was calculated from many reactions, has a high standard deviation (*s* 0.38). Moreover the higher reactivity in electrophilic substitution of the β-position of furan with respect to the β-position of thiophen notwithstanding the σ^+ values has been recently pointed out.[14]

[3] H. H. Jaffè and H. L. Jones, *Adv. Heterocyclic Chem.*, 1964, **3**, 220.

[4] (*a*) A. R. Butler, *J. Chem. Soc.* (*B*), 1970, 867; (*b*) F. Fringuelli, G. Marino, and A. Taticchi, *J.C.S. Perkin II*, 1974, 1738; (*c*) G. Marino, *Adv. Heterocyclic Chem.*, 1971, **13**, 242.

[5] G. T. Bruce, A. R. Cooksey, and K. Morgan, *J.C.S. Perkin II*, 1975, 551 and references therein.

[6] D. S. Noyce and R. L. Castenson, *J. Amer. Chem. Soc.*, 1973, **95**, 1247.

[7] E. A. Hill, M. L. Gross, M. Stasiewicz, and M. Manion, *J. Amer. Chem. Soc.*, 1969, **91**, 7381.

[8] R. D. Brown, A. S. Buchanan, and A. A. Humffray, *Austral. J. Chem.*, 1965, **18**, 1513.

[9] R. Taylor, *J. Chem. Soc.* (*B*), 1968, 1397.

[10] R. Taylor, *J. Chem. Soc.* (*B*), 1970, 1364.

[11] S. Clementi, P. Linda, and G. Marino (*a*) *J. Chem. Soc.* (*B*), 1970, 1153; (*b*) *Tetrahedron Letters*, 1970, 1389; (*c*) G. Ciranni and S. Clementi, *ibid.*, 1971, 3833.

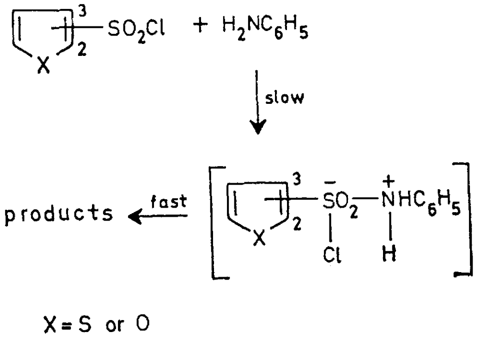
[12] L. W. Deady, R. A. Shanks, and R. D. Topsom, *Tetrahedron Letters*, 1973, 1881.

[13] Ref. 4*c*, p. 275.

[14] R. Taylor, 'Specialist Periodical Reports of the Chemical Society, Aromatic and Heteroaromatic Chemistry,' 1975, p. 220.

[15] (*a*) A. Arcoria, E. Maccarone, G. A. Tomaselli, R. Cali, and S. Gurrieri, *J. Heterocyclic Chem.*, 1975, **12**, 333; (*b*) E. Maccarone, G. Musumarra, and G. A. Tomaselli, *Gazzetta*, 1976, in the press.

[16] (*a*) C. D. Johnson, 'The Hammett Equation,' Cambridge University Press, Cambridge, 1973, p. 103; (*b*) S. Clementi, C. D. Johnson, and A. R. Katritzky, *J.C.S. Perkin II*, 1974, 1294.



Scheme

transition state.[17] This is consistent with the proposed S_AN mechanism [2] which implies the formation of an intermediate complex where the sulphonyl group is negatively charged and the mesomeric interaction between the heteroatom and the reaction centre is lower (see Scheme).

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[17] R. A. Jackson, ' Mechanism,' Clarendon Press, Oxford, 1972, p. 110.