A DETERMINATION OF THE SIGMA ZERO CONSTANT FOR THE PYRIDINE AZA GROUP
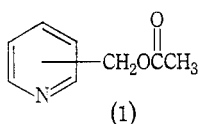
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Hammett σ values[1] for the 2-, 3-, and 4-pyridine aza groups determined from the hydrolysis of pyridyl-methyl acetates,[2] (1), ($\sigma_{2N} = 1 \cdot 1$, $\sigma_{3N} = 1 \cdot 3$, $\sigma_{4N} = 1 \cdot 6$) are all significantly greater than other reported values[3] for these groups. While some variation in aza σ values has been found, especially for the 2-position, there seemed no obvious reason for the considerably enhanced values for all three positions found by Simonetta and Favini for this reaction.

As part of a study of factors affecting aza σ values, we have investigated this alkaline hydrolysis in 56% (w/w) acetone–water at 25°, and obtained results indicating close agreement between σ values required for this reaction and for hydrolysis of methyl pyridinecarboxylates.[4] The σ values for aza and nitro groups are as follows:[4-8]

	2_N	3_N	4_N	3_{nitro}	4_{nitro}
σ	$0 \cdot 75$ [4]	$0 \cdot 65$ [4]	$0 \cdot 96$ [4]	$0 \cdot 71$ [5]	$0 \cdot 78$ [5]
σ^0	$0 \cdot 81$	$0 \cdot 72$	$0 \cdot 95$	$0 \cdot 70$ [6]	$0 \cdot 82$ [6]
σ_R^0	$0 \cdot 27$ [7]	—	—	$0 \cdot 19$ [8]	—

We have found[9] that aza σ values established for this latter hydrolysis in methanol–water are also applicable in aqueous acetone and dioxan solvents.

The previous study used dioxan–water solvent and established $\rho = 0 \cdot 25$ at 20° from hydrolysis of a limited series of substituted benzyl acetates. Extensive data

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(12 substituents) on this reaction in 56% (w/w) acetone–water are available[10] and Jaffe calculated[11] $\rho = 0 \cdot 743$ from these results, though the correlation using σ values ($r = 0 \cdot 965$) was not good. However, reactions of this type of compound, where there can be no direct conjugation between substituent and reaction site, require σ^0 (see[6]) rather than σ parameters. The correlation is indeed improved by use of σ^0 values. We obtained $\log k_2 = 0 \cdot 73\sigma^0 - 1 \cdot 20$ ($r = 0 \cdot 993$, $s = 0 \cdot 031$) and used this to calculate the effective pyridine aza σ^0 values. The rate constants k_2 (l. mol^{-1} s^{-1}) for the alkaline hydrolysis of substituted methyl acetates (RCH_2COCH_3) in acetone–water (56% w/w) at 25° are as follows: R = phenyl, $0 \cdot 0693$ (cf.[10] $0 \cdot 0696$); R = 2-pyridyl, $0 \cdot 244$; R = 3-pyridyl, $0 \cdot 213$; R = 4-pyridyl, $0 \cdot 311$. The derived σ^0 values are in the tabulation above.

It can be seen that under these conditions there is no significant difference between the σ and σ^0 values for the aza groups. This is also the case with the aromatic nitro group and the similar behaviour is to be expected since both substituents are strongly electron withdrawing predominantly through inductive effects.

The 2-aza group has generally been included in Hammett treatments[3] since steric effects are minimal with this substituent. It is of interest regarding the origin of the electronic effect of this *ortho* substituent that the σ and σ^0 values are virtually the same. The distance between substituent and reaction site is considerably greater in the benzyl acetate than in the methyl benzoate and any "proximity effects" contributing to the σ value would be less in the former compound.

Experimental

Esters

2-Pyridylmethyl acetate, b.p. 74°/0·7 mm, and 4-pyridylmethyl acetate, b.p. 78°/0·7 mm, were prepared by reaction of acetic anhydride with the appropriate picoline 1-oxide.[12] Careful fractionation was required in each case to separate (as indicated by g.l.c. and n.m.r.) the pure compound from the isomeric by-product, e.g., 3-acetoxy-4-picoline.

Benzyl acetate, b.p. 55°/0·3 mm, and 3-pyridylmethyl acetate, b.p. 87°/2 mm, were prepared by acetylation of the corresponding alcohols.

Kinetics

The method has been discussed previously.[13]

Acknowledgment

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