A Re-evaluation of the Hammett σ_p Values for the Hydroxymethyl and Formyl Groups

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The Hammett constant σ_p for the hydroxymethyl group is estimated as -0.04 ± 0.03, and that for the formyl group is re-evaluated as $+0.57 \pm 0.07$.

CORNISH and EABORN [1] have proposed recently the relationships (i) and (ii) concerning the Hammett constant $\sigma_p(CH_2Y)$. These relationships have been tested with good agreement for two groups (Y = CN or OMe) for which experimental data were available. Applied to the group CH_2OH (Y = OH) they lead to the

$$\sigma_p(CH_2Y) = -0.11 + 0.5\sigma_p(Y) \qquad (i)$$

results: $\sigma_p(CH_2OH) = +0.04$ and $+0.07$, from equations (i) and (ii), respectively.

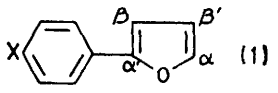
In a recent study [2] of the transmission of electronic effects by the furan ring, we have found good correlations

$$\sigma_p(CH_2Y) = \sigma_p^+(CH_2Y) + 0.06 \qquad (ii)$$

between $\delta(^{13}C)$ and σ_p [equation (iii)] for the carbon-atoms of the heterocycle in compounds of type (1). The parameters of equation (iii) for the four carbon

$$\delta(^{13}C) = \delta_0 + \rho\sigma_p(X) \qquad (iii)$$

atoms of the furan ring are summarized in the Table, which also gives the shifts for $X = CH_2OH$ and the deduced σ_p values. It appears that these correlations give the best value of $\sigma_p(CH_2OH)$ in the case of C_β, *i.e.*



(1)

-0.05 ± 0.02. As this value is not exactly the same as that calculated by Eaborn, we undertook a direct determination by means of the pK value. Using the potentiometric method of Albert and Serjeant,[3] we obtained for *p*-hydroxymethylbenzoic acid (HMBA) in water at 25 °C a pK value of 4.16 ± 0.03. The pK value of benzoic acid (BA) was also measured,[4] and gave the same result as in ref. 3, *i.e.* 4.12 ± 0.01. Hence $\sigma_p(CH_2OH)$ [= pK(BA) − pK(HMBA)] = -0.04 ± 0.03, which agrees well with the value from n.m.r. data.

The established value [5] of σ_p(CHO) (+0.45) appears too small in view of our n.m.r. data,[2] which suggest a value of $+0.57 \pm 0.07$. This value is inferred from $\delta(^{13}C_\beta)$, which gives a better correlation than $\delta(^{13}C_\alpha)$

Parameters of equation (iii) *

	δ_0	ρ	r^2	$\delta(^{13}C)$ for $X = CH_2{\cdot}OH$	$\sigma_p(CH_2OH)_{calc.}$
C_α	142.07	2.24	0.963	141.80	−0.12
	±0.08	±0.18			±0.10
C_β	105.08	4.76	0.958	104.82	−0.05
	±0.2	±0.4			±0.02
$C_{\alpha'}$	153.56	−2.20	0.852	153.62	−0.02 †
$C_{\beta'}$	111.72	0.598	0.843	111.46	‡

* Uncertainties in δ_0 and ρ values are classical determinations resultingfrom regression analysis (N. R. Draper and H. Smith, 'Applied Regression Analysis,' Wiley, New York, 1966), and were obtained by using a Hewlett–Packard Hp–55 computer. † Greater imprecision than for C_α [smaller r^2 value, with the same slope (W. H. Davis, jun., and W. A. Pryor, *J. Chem. Educ.*, 1976, **53**, 285)]. ‡ Too small a ρ value for determination of σ_p.

[corresponding to σ_p(CHO) = $+0.61 \pm 0.12$]. This new evaluation of σ_p(CHO) is satisfactory in comparison with values for similar electron-withdrawing groups such as COMe (+0.502) and CO_2Et (+0.45).[4]

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