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CORRELATION OF DETRITIATION PARTIAL RATE FACTORS WITH CALCULATED σ^+ VALUES.

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Dewar and Grisdale (1) have developed a method for estimating the values of Hammett σ- constants, in which the "inductive" effect of substituents is replaced by a field effect. Good correlation is obtained between their calculated σ values and both the pK values of substituted 1- naphthoic acids and the changes in infrared carbonyl frequencies of methyl 1- naphthoates, where there is no mutual conjugation between the substituent and the reaction center.

For reactions such as the detritiation of substituted 1- tritio naphthalenes, as reported by Bott, Spillett and Eaborn (2), conjugation is possible between the substituent and the reaction center. Their partial rate factors do not correlate well with Dewar and Grisdale's (1) calculated σ values. Fig. 1.

We wish to point out that an excellent correlation may be obtained (Fig. 2) if Dewar and Grisdale's method (1) is modified in the following way: σ^+ constants, instead of σ constants, are calculated from either I or II

$$\sigma_{ij}^{+} = F^{+}/r_{ij} + M^{+}q_{ij} \quad \ldots\ldots\ldots\ldots\ldots(I)$$

$$\sigma_{ij}^{+} = (F^{+})'/r_{ij} + (M^{+})'\pi_{ij} \quad \ldots\ldots\ldots\ldots(II)$$

where F^+ or $(F^+)'$ is a measure of the field set up by the substituent, r_{ij} is the distance between atoms i and j in units of one aromatic bond length (1), q_{ij} is the formal charge at position j produced by attaching the group $-CH_2^-$ at position i, π_{ij} is the atom-atom polarisabilities of atoms i and j, and M^+ or $(M^+)'$ is a measure of the combined π - inductive, mesomeric and electromeric effects of the substituents.

The constants F^+, M^+ or $(F^+)'$, $(M^+)'$ are obtained from σ^+_{meta} and σ^+_{para} for benzene (3), and σ^+ constants for any other system can then be calculated. Those for positions in naphthalene are shown in Table 1.

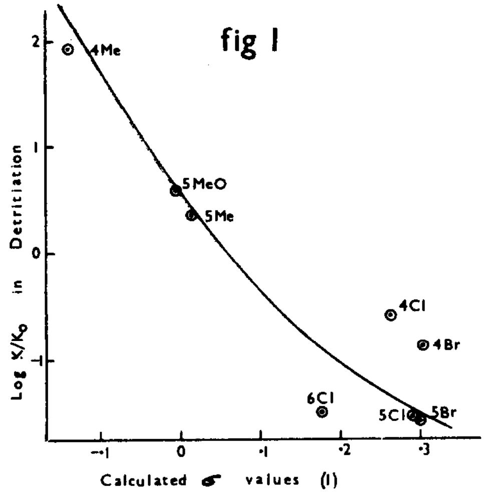

fig 1

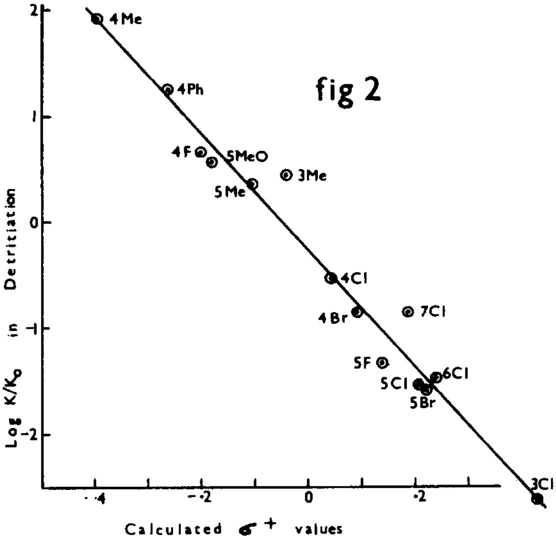

fig 2

The success of this treatment indicates, as has been previously suggested (4) that the electromeric effect, as it operates in detritiation reactions, varies with distance in much the same way as the mesomeric and π - inductive effects.

Work is in progress to obtain substituent effect data for systems other than naphthalene, to see if similar correlations may be obtained.

TABLE 1.

σ^+_{ij}	F	Cl	Br	Me	MeO	Ph
σ^+_{21}	(-0.182)	(0.208)	(0.285)	(-0.339)	(-1.549)	
σ^+_{31}		0.400 (0.420)		-0.066 (-0.046)		
σ^+_{41}	-0.224 (-0.204)	0.021 (0.034)	0.075 (0.082)	-0.433 (-0.398)	-1.106 (-1.215)	0.289 (-0.273)
σ^+_{51}	0.099 (0.131)	0.181 (0.201)	0.196 (0.213)	-0.132 (-0.110)	-0.256 (-0.184)	
σ^+_{61}		0.231 (0.235)				
σ^+_{71}		0.181 (0.180)				
σ^+_{81}		(0.438)				

σ^+ Constants Calculated by F^+ M^+ $^{(a)}$, ($F^{+'}$ $M^{+'}$) $^{(b)}$ Methods (1) for positions in Naphthalene for which Detritiation results are available (2).

(1) M.J.S. Dewar and P.J. Grisdale, *J. Am. Chem. Soc.* **84**, 3548 (1962)

(2) R.W. Bott, R.W. Spillett and C. Eaborn, *Chem. comm.*, 1965, 147.

(3) L. Stock and H.C. Brown, *Advances in Physical Organic Chemistry*, Vol.I, p96. Academic Press, London (1963)

(4) M.J.S. Dewar. *J. Am. Chem. Soc.* **74**, 3350 (1952)