Substituent Effects and Excited State Reactivity [1]

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Analysis of published data on excited singlet reactivity shows that a new set of substituent constants, σ_{ex}, gives significantly better correlations than σ. Some properties and limitations of the new constants are discussed.

RECENTLY, we published calculations indicating differences in substituent effects in different singlet excited states of 1-arylbutadienes.[2] However, reported experimental reactivity data on excited states have generally been analysed in terms of ground-state substituent constants, σ, σ^+, or σ^-, implying that substituent effects are not affected by changing the electronic state. Two reports [3,4] consider differences between ground-state and excited-state substituent constants, but in each case only a limited range of substituents was considered, and no evidence was given that the excited state constants have any general usefulness; indeed, the results of Sengupta and Lahiri,[3] applying their constants to phenol pK_a*, suggest that they do not. The present study was carried out firstly to determine whether a sufficiently large amount of reliable reactivity data are available to set up a scale of excited-state substituent constants, and secondly to determine whether the resulting constants show any significant improvement over the ground-state constants previously used, when correlating excited state reactivity.

Reported data on excited-state reactivity are most readily available for singlet acidities,[5] and a particularly large number of results are available for the pK_a* values of phenols. Three methods have been used for determining pK_a*: Förster cycle [6] applied to absorption maxima of acidic and basic forms, Förster cycle applied to 0–0 frequencies (estimated as average of absorption maximum and fluorescence maximum) of acidic and basic forms, and analysis of the pH dependence of fluorescence intensity.[7] Of these, the first has been used most often (it is often the only method available when one or both forms do not fluoresce), but has no theoretical justification, and results of this method often differ by one or more pK_a units from results obtained by other methods.[†,9] The other two methods are generally in better agreement. For the pK_a* of phenols, values obtained by Förster cycle on 0–0 bands or by pH dependence of fluorescence have been reported for a wide range of substituents, and these values were used to derive the excited-state substituent constants σ_{ex}. In Table 1, pK_a* values are given for 16 phenols; least-squares analysis of pK_a* against σ gave $\rho = -3.10$. We define σ_{ex} so as to have the same ρ value; this will result in substituent constants which can most readily be compared with ground-state constants:

$$\sigma_{ex} = (pK_a^* - 3.804)/-3.10$$

where pK_a* refers to the corresponding phenol.

Two important substituents, cyano and nitro, were not included, because fluorescence data are not available. Approximate σ_{ex} values are given in Table 2, obtained from Förster cycle on absorption maxima. The other values in Table 2 refer to substituents for which pK_a*

TABLE 1

pK_a* of phenols and σ_{ex}

Substituent	Reported pK_a* [a]	avg. pK_a*	σ [b]	σ_{ex} [c]
H	4.0,[d] 3.62,[e] 4.1,[f] 3.6,[g] 3.7 [h]	3.084	0	0
3-F	3.8 [d]	3.8	0.337	0
4-F	4.4,[d] 3.5 [e]	3.95	0.062	−0.05
3-Cl	3.0,[d] 4.0 [e]	3.5	0.373	0.10
4-Cl	3.2,[d] 3.5,[e] 2.6 [h]	3.1	0.227	0.23
3-Br	2.8 [d]	2.8	0.391	0.32
4-Br	3.1,[d] 2.9,[e] 2.9,[f] 3.0,[i] 3.1 [j]	3.0	0.232	0.26
3-OMe	4.6,[d] 2.7,[e] 4.6,[f] 3.4,[h] 4.8,[i] 4.6 [j]	4.12	0.115	−0.10
4-OMe	5.6,[d] 4.7,[e] 5.7,[f] 4.1 [h]	5.025	−0.268	−0.39
3-Me	4.0,[d] 4.2 [e]	4.1	−0.069	−0.10
4-Me	4.3,[d] 4.1,[e] 3.7,[h] 4.6,[i] 4.3 [j]	4.2	−0.170	−0.13
3-Et	4.1,[d] 4.5 [e]	4.3	−0.043 [k]	−0.16
4-Et	4.3,[d] 4.3 [e]	4.3	−0.151 [k]	−0.16
$3-CF_3$	1.5 [g]	1.5	0.43	0.74
$4-CF_3$	2 [g]	2	0.54	0.58
$4-NMe_3^+$	1.7,[d] 1.6,[f] 1.6,[i] 1.7 [j]	1.65	0.82	0.69

[a] Förster cycle on absorption maxima not included. In notes, FC = Förster cycle on 0–0 frequencies and fl = pH dependence of fluorescence. [b] C. Laurence and B. Wojtkowiak, *Ann. Chim.* (14*me Sér.*), 1970, **5**, 163. [c] See text for definition. [d] FC from E. L. Wehry and L. B. Rogers, *J. Amer. Chem. Soc.*, 1965, **87**, 4234. [e] FC from W. Bartok, R. B. Hartman, and P. J. Lucchesi, *Photochem. Photobiol.*, 1965, **4**, 499. [f] FC from E. L. Wehry and L. B. Rogers, *J. Amer. Chem. Soc.*, 1966, **88**, 351. [g] FC ref. 11. [h] fl ref. 10. [i] fl ref. 9. [j] FC ref. 9. [k] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 1957, **79**, 1913.

of the phenol is available, but no other excited-state reactivity data have been reported, so these substituent constants were not used in any other correlations. Some substituents for which phenol pK_a* data are available (for example CO_2H, NH_2) have been omitted because the measured pK_a* probably does not correspond to proton removal from the phenolic OH in the excited state.

To determine the usefulness of the new constants, σ_{ex}, other excited-state reactivity data were analysed as a function of σ and of σ_{ex}. Table 3 shows the results of least-squares correlations. It is clear from the correlation coefficients that the constants σ_{ex} generally give better linear correlation than σ, and, therefore, consistently give a better description of the transmission of

† Values of pK_a* for phenols from Förster cycle on absorption maxima were taken from ref. 8.

TABLE 2

pK_a^* of phenols and σ_{ex}

Substituent	Reported pK_a^* [a]	Avg. pK_a^*	σ [b]	σ_{ex} [c]
4-CN	−1.27 [d]	−1.27	0.660	1.6
3-NO_2	−1.14,[e] −1.12,[f] −2.18,[g] −1.20 [h]	−1.41	0.710	1.7
4-NO_2	−4.28,[e] −6.65,[f] −5.78,[g] −6.74 [h]	−5.86	0.778	3.1
3-OEt	4.4 [i]	4.4		−0.19
4-OEt	5.3 [i]	5.3		−0.48
4-SO_3^-	2.4,[i] 2.3,[j] 2.6,[k] 2.4 [l]	2.43		0.44
3-CH_2OH	3.0 [m]	3.0		0.26
4-CH_2OH	3.0 [m]	3.0		0.26
3-OH	3.8 [n]	3.8		0
4-OH	3.1 [n]	3.1		0.23
3-SO_2Me	2.6 [o]	2.6		0.39
4-SO_2Me	2.3 [o]	2.3		0.49
4-SO_2Ph	2.1 [o]	2.1		0.55
3-SOMe	2.8 [o]	2.8		0.32
4-SOMe	2.4 [o]	2.4		0.45
4-SOPh	2.3 [o]	2.3		0.49
3-SMe	4.4 [o]	4.4		−0.19
4-SMe	4.4 [o]	4.4		−0.19
3-SPh	4.4 [o]	4.4		−0.19
4-SPh	4.2 [o]	4.2		−0.13
3-$SMe_2^+Cl^-$	2.2 [o]	2.2		0.52
4-$SMe_2^+Cl^-$	2.0 [o]	2.0		0.58

[a] In notes, FC(abs) = Förster cycle on absorption maxima, FC(00) = Förster cycle on 0–0 frequencies, fl = pH dependence of fluorescence. [b] C. Laurence and B. Wojtkowiak, *Ann. Chim.* (14*me Sér.*), 1970, **5**, 163. [c] See text for definition. [d] FC(abs) calc. from u.v. of G. P. Scheimenz, *Spectrochim. Acta*, 1968, **A24**, 465; and pK_a from J. P. Dupont, J. D'Hondt, and T. Zeegers-Huyskens, *Bull. Soc. Chim belges*, 1971, **80**, 369. [e] FC(abs) calc. from u.v. of S. D. Hamann, *J. Phys. Chem.*, 1966, **70**, 2418. [f] FC(abs) from S. D. Hamann and M. Linton, *Austral. J. Chem.*, 1975, **28**, 701. [g] FC(abs) recalc. from S. G. Schulman, L. B. Sanders, and J. D. Winefordner, *Photochem. Photobiol.*, 1971, **13**, 381, using pK_a of E. L. Wehry and L. B. Rogers, *J. Amer. Chem. Soc.*, 1966, **88**, 351. [h] FC(abs) calc. from u.v. of L. Doub and J. M. Vandenbelt, *J. Amer. Chem. Soc.*, 1947, **69**, 2714; 1949, **71**, 2414; 1955, **77**, 4535, and pK_a of E. L. Wehry and L. B. Rogers, *J. Amer. Chem. Soc.*, 1966, **88**, 351. [i] FC(00) from E. L. Wehry and L. B. Rogers, *J. Amer. Chem. Soc.*, 1965, **87**, 4234. [j] FC(00) from E. L. Wehry and L. B. Rogers, *J. Amer. Chem. Soc.*, 1966, **88**, 351. [k] fl from ref. 9. [l] FC(00) from ref. 9. [m] FC(00) from W. Bartok, R. B. Hartman, and P. J. Lucchesi, *Photochem. Photobiol.*, 1965, **4**, 499. [n] fl from ref. 10. [o] FC(00) from ref. 4.

substituent effects through an excited-singlet benzene ring.†

The uncertainty in the new substituent constants is rather large. Errors are not generally quoted in the pK_a^* values used in this study, but they can be roughly estimated: 0.5 nm wavelength error in the absorption and fluorescence maxima results in an error in the Förster cycle calculations of pK_a^* of 0.1—0.15 units in the region of the spectrum appropriate to most phenols. Errors in the determination of pK_a^* by pH dependence of fluorescence are quoted as 0.1—0.2 units by Avigal *et al.*,[10] and there is a spread of values averaging 0.15 pK_a units for different reports using the same method. Thus the average pK_a^* values may be accurate to only *ca.* 0.3 units, giving an uncertainty of *ca.* 0.1 in the values of σ_{ex}. Values for CN and NO_2 are rather less reliable, since values from the Förster cycle on absorption maxima may differ from values obtained by other methods by about 1.5 pK_a units,[8,9] and the probable error in these values of σ_{ex} is around 0.5. The pK_a^* of 4-trifluoromethylphenol is approximate,[11] and a larger error applies to σ_{ex} for this substituent. Similar uncertainties apply to the pK_a^* data in Table 3, in fact most of them are obtained by Förster cycle on absorption data, and in view of this the first five correlations with σ_{ex} are quite reasonable.

† The two exceptions have only a small number of substituents, all in the same position. Correlation with σ in other cases improves if 3- and 4- substituents are considered separately.

In comparing σ and σ_{ex} values in Tables 1 and 2, it is convenient to consider three types of substituent. (i) Purely inductive and hyperconjugative substituents (Me, Et, CF_3, and NMe_3^+) have similar values of σ and σ_{ex}. (ii) Mesomerically electron-donating substituents with lone pairs (halogens, OMe, and OEt) have similar σ and σ_{ex} in the 4-position, but σ_{ex} is more negative by 0.1 to 0.3 units than σ for the 3-position. This extra electron-donating effect of 3-substitution is largely responsible for the greater success of σ_{ex} in correlating data referring to both 3- and 4-substituents, and is in agreement with our calculated electron densities in 1-arylbutadienes.[2] (iii) Mesomerically electron-withdrawing substituents (CN and NO_2) have very large values of σ_{ex}. This is particularly striking in all the pK_a^* data analysed, and is consistent with qualitative observations, for example on photosubstitution reactions.

TABLE 3

Correlations of excited state reactivity [a]

Reaction	n	With σ ρ	With σ r	With σ_{ex} ρ	With σ_{ex} r
pK_a^* of 4-styrylpyridines [b]	8	−6.50	0.883	−2.15	0.982
pK_a^* of 2-styrylpyridines [b]	8	−6.92	0.915	−2.16	0.959
pK_a^* of $ArCO_2H$ [c]	9	−5.31	0.856	−1.82	0.971
pK_a^* of $ArCO_2H$ [d]	8	−7.41	0.854	−1.93	0.967
pK_a^* of 2-nitroanilines	11	−7.31	0.784	−3.02	0.941
pK_a^* of 3-nitroanilines [f]	4	−5.84	0.801	−2.03	0.691
pK_a^* of anilines [d]	11	−1.15	0.181	−2.91	0.438
pK_a^* of acetophenones [g]	5	−3.02	0.554	−3.19	0.694
log k for $Ar_2C{=}CHCHR_2$ photorearrangement [h]	5	3.47	0.856	1.59	0.733

[a] n = no. of substituents, including H; r is least-squares correlation coefficient. [b] J. C. Doty, J. L. R. Williams, and P. J. Grisdale, *Canad. J. Chem.*, 1969, **47**, 2355. [c] Calc. by Förster cycle from u.v. of L. Doub and J. M. Vandenbelt, *J. Amer. Chem. Soc.*, 1947, **69**, 2714; 1949, **71**, 2414; 1955, **77**, 4535; and pK_a of J. M. Vandenbelt, C. Henrich, and S. G. Vanden Berg, *Analyt. Chem.*, 1954, **26**, 726 (measured by u.v.). [d] Ref. 3. [e] J. P. Idoux and C. K. Hancock, *J. Org. Chem.*, 1968, **33**, 3498. [f] See ref. given in footnote *e*; substituents in 5-position only. [g] Ref. 5. [h] S. S. Hixson, *J.C.S. Chem. Comm.*, 1975, 515; 4-substituents only, and two of the five rate constants are order-of-magnitude estimates.

When these constants are used for mechanistic study, the low accuracy of σ_{ex} must be taken into account. Thus it may be necessary to use a fairly large number of substituents to obtain a significant difference between correlations using σ_{ex} and correlations using σ or other ground-state constants. Use of both 3- and 4-substituents is desirable, particularly F, Cl, OMe, or OEt, and the large effects of CN and NO_2 substituents may be useful, though with nitro-compounds particularly, changes in reaction type may occur. Provided these points are borne in mind, the differences between σ and σ_{ex} should be useful in mechanistic studies.

Finally we consider some limitations of the constants σ_{ex}. A major problem facing the correlation of excited-state reactivities is the low accuracy of the data. It is difficult to imagine any great improvement in Förster cycle accuracy while broad absorption and emission bands must be used, and in any case the assumption $\Delta S = \Delta S^*$ may be a limitation on the accuracy of the results. Results based on equilibrium or kinetic measurements of protonation and deprotonation in the excited state can in principle be improved, but the assumption of the attainment of equilibrium during the lifetime of the excited state may limit the accuracy, although recent work [12] suggests that this assumption may be justified. Moreover, the effects of diffusion rates may introduce errors here, as they have been shown to do in exciplex kinetics.[13] Thus the values of σ_{ex}, and the data to be correlated, are likely to remain relatively inaccurate.

A second serious limitation of any substituent constants in excited states is that substitution also affects the rates of photophysical processes, in a manner depending more on available vibration modes than on any electron donating or withdrawing effects. Therefore, it may not be possible in some cases to make any use of substituent constants.[14]

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