# Reliable $\sigma^+$ Values for Some Strong Resonance Donor Substituents

By **Sergio Clementi** and **Paolo Linda,*** Istituto di Chimica Organica, Università di Perugia, 06100 Perugia, Italy

Reliable $\sigma^+$ constants for some strong resonance donor substituents are evaluated by the Extended Selectivity Treatment leading to the following values: $\sigma^+_{p\text{-OH}} = -0{\cdot}92$, $\sigma^+_{p\text{-OPh}} = -0{\cdot}56$, $\sigma^+_{p\text{-NHCOMe}} = -0{\cdot}69$, $\sigma^+_{p\text{-NH}_2} = -1{\cdot}31$, and $\sigma^+_{p\text{-NMe}_2} = -1{\cdot}50$.

$\sigma$ VALUES can be obtained either from a reference reaction or by a statistical approach applied to the available data. A complete statistical framework of the Hammett equation was recently developed,[1] and suggested as the best way of estimating substituent constants, since no reaction is theoretically better suited to be a standard. On the other hand, statistical values are always dependent on the body of knowledge at the time of evaluation and can never be ' final '. Therefore a statistical approach should be reliable when a large amount of data is available, which is probably not the case for the time being, at least for some substituents in individual $\sigma$ scales.

For the case of aromatic electrophilic substitution, $\sigma^+$ values were determined by Brown and his co-workers from the solvolysis rate data of 2-arylpropyl chlorides[2] and then tested statistically by the ' Extended Selectivity Treatment ' (EST).[3,†]

The results from the EST obviously depend on the

TABLE 1

log (Partial rate factors) for electrophilic reactions of phenol, diphenyl ether, acetanilide, aniline, and *NN*-dimethylaniline

| No. | Reaction | $\rho$ | OH | OPh | NHCOMe | $NH_2$ | $NMe_2$ |
|---|---|---|---|---|---|---|---|
| 1 | Pyrolysis of 1-arylethyl acetates, 327° | $-0{\cdot}66$ [a] | | $0{\cdot}35$ [b] | | | |
| 2 | Ionisation of $Ar_3COH$, aq. $H_2SO_4$, 25° [c] | $-3{\cdot}5$ [d] | $2{\cdot}87$ [e] | | $1{\cdot}62$ [e] | $4{\cdot}73$ [f] | $5{\cdot}33$ [f] |
| 3 | Protodegermylation of $ArGeEt_3$, $HClO_4$, MeOH–$H_2O$, 50° | $-3{\cdot}9$ [g] | $3{\cdot}44$ [g] | $1{\cdot}59$ [g] | | | $6{\cdot}48$ [g] |
| 4 | Solvolysis of benzhydryl chlorides, EtOH, 25° | $-4{\cdot}0$ [h] | | $2{\cdot}33$ [h] | | | |
| 5 | Mercuriation, $Hg(AcO)_2$, AcOH, 25° | $-4{\cdot}0$ [i] | | $2{\cdot}29$ [j] | $2{\cdot}44$ [j] | | |
| 6 | Protodesilylation of $ArSiMe_3$, $HClO_4$, MeOH–$H_2O$, 51° | $-4{\cdot}3$ [d] | $4{\cdot}03$ [k] | $1{\cdot}95$ [l] | | | $7{\cdot}48$ [k] |
| 7 | Ionisation of $Ar_2CHOH$, aq. $H_2SO_4$, 25 [c] | $-4{\cdot}7$ [d] | | $1{\cdot}73$ [e] | | | $9{\cdot}46$ [f] |
| 8 | Solvolysis of 1-arylethyl acetates, 30% EtOH, 25° | $-5{\cdot}7$ [m] | | $2{\cdot}80$ [m] | | | $9{\cdot}81$ [m] |
| 9 | Solvolysis of 1-arylethyl chlorides, 50% EtOH, 25° | $-5{\cdot}7$ [n] | | $3{\cdot}40$ [o] | | | |
| 10 | Hydrogen exchange, aq. $H_2SO_4$, 100°, pH = 0 | $-7{\cdot}5$ [p] | $7{\cdot}00$ [p] | | | $9{\cdot}76$ [p] | $11{\cdot}08$ [p] |
| 11 | Protodetritiation, $CF_3CO_2H$, 70° | $-8{\cdot}5$ [p,q] | | $4{\cdot}49$ [r] | | | |
| 12 | Chlorination, $Cl_2$, AcOH, 25° | $-10{\cdot}0$ [i] | | | $6{\cdot}40$ [s] | | |
| 13 | Bromination, $Br_2$, $H_2O$, 25° | $-11{\cdot}6$ [t] | $10{\cdot}18$ [t] | | | | $13{\cdot}91$ [u] |
| 14 | Bromination, $Br_2$, AcOH, 25° | $-12{\cdot}1$ [i] | $11{\cdot}82$ [v] | $7{\cdot}60$ [v,w] | $9{\cdot}08$ [v] | | $19{\cdot}50$ [v] |

[a] R. Taylor, G. G. Smith, and W. H. Wetzel, *J. Amer. Chem. Soc.*, 1962, **84**, 4817. [b] Ref. 8. [c] $\Delta pK$ Values. [d] Ref. 2. [e] Ref. 9. [f] Ref. 10. [g] Ref. 11. [h] Ref. 12. [i] Ref. 4. [j] Ref. 13. [k] Ref. 14. [l] Ref. 15. [m] Ref. 16. [n] Calculated from data in ref. 17, exlcuding OMe. [o] Ref. 17. [p] Ref. 18. [q] R. Baker, C. Eaborn, and R. Taylor, *J.C.S. Perkin II*, 1972, 97. [r] Ref. 19 [s] Ref. 20. [t] Ref. 21. [u] Ref. 22. [v] Ref. 23. [w] This value was reported in ref. 4 without correction for the statistical factor.

---

† In the EST the statistical framework is involved twice, since $\rho$ values are by themselves statistical parameters. They were first evaluated[3] by plotting log $f$ for the reaction concerned against log $f$ for the standard reaction; only the data available at the time were obviously used, whereas they might be now recalculated to include many more data.

[1] S. Wold and M. Sjöström, *Chemica Scripta*, 1972, **2**, 49.

[2] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4979.

[3] H. C. Brown and L. M. Stock, *J. Amer. Chem. Soc.*, 1962, **84**, 3298.

number of available data; nevertheless good agreement was found between the figures obtained from these two approaches.[4]

The $\sigma^{+}_{p}$ values for some strong resonance donor groups (OH, OPh, NHCOMe, $NH_2$, and $NMe_2$ are dealt with in this paper) were not evaluated by the standard reaction, mostly because of the 'facile' hydrolysis of the chlorides involved. They were reported in later reviews [5-7] as inaccurate, referring to a roughly weighted average of a few electrophilic reactivity data as $\sigma^{+}_{p\text{-OH}} = -0{\cdot}92$, $\sigma^{+}_{p\text{-OPh}} = -0{\cdot}5$, $\sigma^{+}_{p\text{-NHOOMe}} = -0{\cdot}6$, $\sigma^{+}_{p\text{-NH}_2} = -1{\cdot}3$, and $\sigma^{+}_{p\text{-NMe}_2} = -1{\cdot}7$.[2,*] Since more reliable values are needed for our studies in electrophilic substitution of heteroaromatic compounds, the EST was applied to all the available data for these substituents.

## RESULTS AND DISCUSSION

All the log (partial rate factors) listed in Table 1 were available in the literature or were calculated from reported data.[8-23]

The regression data, summarised in Table 2, were evaluated by an equation restricted to go through the origin.[24]

The values obtained for OH and $NH_2$ are coincidental with those used so far, *i.e.* $-0{\cdot}92$ and $-1{\cdot}31$ respectively, whereas the $\sigma_{p}^{+}$ constants for the phenoxy- ($-0{\cdot}56$) and the acetamido- ($-0{\cdot}69$) groups are slightly more negative than the old averages, the correlation coefficients always being satisfactory.

On the other hand $\sigma^{+}_{p\text{-NMe}_2}$ is calculated as $-1{\cdot}50$ instead of $-1{\cdot}70$. The actual figure is significantly less negative, thus becoming closer to $\sigma^{+}_{p\text{-NH}_2}$. However, this smaller value appears to be more reliable, since the additional activating effect due to the methyl groups cannot be expected to be very large because of incomplete resonance through the nitrogen atom.

TABLE 2

$\sigma^{+}_{p}$ Values and regression data from EST

| Group | $\sigma^{+}_{p}$ | $n$ [a] | $r$ [b] |
|---|---|---|---|
| OH | $-0{\cdot}92$ | 6 | 0·999 |
| OPh | $-0{\cdot}56$ | 10 | 0·990 |
| NHCOMe | $-0{\cdot}69$ | 4 | 0·994 |
| $NH_2$ | $-1{\cdot}31$ | 2 | 1·000 [c] |
| $NMe_2$ | $-1{\cdot}50$ | 8 | 0·989 |

[a] Number of points. [b] Correlation coefficient. [c] This value, rounded to the third decimal place, is really less than unity, since a theoretical origin treatment involves one more point.

Although we realize that these figures are only better estimates of the substituent constants and not the 'true' values we do believe that they may be used with more confidence than the older averages and henceforth they may be treated together with $\sigma^{+}$ values derived from the standard solvolysis reaction.

We thank Professor G. Marino for helpful discussions.

[3/762 *Received*, 10th *April*, 1973]

---

[*] Moreover, unfortunately, $\sigma^{+}_{p\text{-NHCOMe}}$ is probably misprinted in ref. 5 as 0·00.

[4] L. M. Stock and H. C. Brown, *Adv. Phys. Org. Chem.*, 1963, **1**, 35.

[5] C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, 1964, **2**, 323.

[6] C. Laurence and B. Wojtkowiak, *Ann. Chim.*, 1970, **5**, 163.

[7] O. Exner, 'The Hammett Equation,' in N. B. Chapman and J. Shorter, 'Advances in Linear Free-Energy Relationships,' Plenum Press, London, 1972.

[8] R. Taylor, *J. Chem. Soc.* (*B*), 1971, 1450.

[9] N. C. Deno and W. L. Evans, *J. Amer. Chem. Soc.*, 1957, **79**, 5804.

[10] N. C. Deno and A. Schriesheim, *J. Amer. Chem. Soc.*, 1955, **77**, 3051.

[11] C. Eaborn and K. C. Pande, *J. Chem. Soc.*, 1961, 297.

[12] J. Packer, J. Vaughan, and A. F. Wilson, *J. Org. Chem.*, 1958, **23**, 1215.

[13] H. C. Brown and M. Dubeck, *J. Amer. Chem. Soc.*, 1960, **82**, 1939.

[14] C. Eaborn, *J. Chem. Soc.*, 1956, 4858.

[15] C. Eaborn and J. A. Sperry, *J. Chem. Soc.*, 1961, 4921.

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

[17] V. J. Shiner, jun., W. Buddembaum, B. L. Murr, and G. Lamaty, *J. Amer. Chem. Soc.*, 1968, **90**, 418.

[18] S. Clementi and A. R. Katritzky, *J.C.S. Perkin II*, 1973, 1077.

[19] R. Baker and C. Eaborn, *J. Chem. Soc.*, 1961, 5077.

[20] P. B. D. de la Mare and M. Hassan, *J. Chem. Soc.*, 1958, 1519.

[21] J.-E. Dubois, J. J. Aaron, P. Alcais, J. P. Doucet, F. Rothenberg, and R. Uzan, *J. Amer. Chem. Soc.*, 1972, **94**, 6823.

[22] R. Uzan and J.-E. Dubois, *Bull. Soc. chim. France*, 1971, 598.

[23] P. B. D. de la Mare, *J. Chem. Soc.*, 1954, 4450.

[24] C. A. Bennett and N. L. Franklin, 'Statistical Analysis in Chemistry and the Chemical Industry,' Wiley, New York, 1954, p. 232.