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RELATIONSHIPS BETWEEN ELECTRONIC SUBSTITUENT PARAMETERS

LEIF J. SÆTHRE*

Department of Chemistry, Institute of Mathematical and Physical Sciences, University of Tromsø, N-9000 Tromsø, Norway

AND

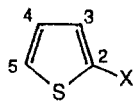
T. DARRAH THOMAS

Department of Chemistry and Center for Advanced Materials Research, Oregon State University, Corvallis OR 97331-4003, U.S.A.

Core-electron energies for sulphur in a series of 2-substituted thiophenes have been used to investigate the relationship between electronic substituent parameters as developed by Taft and Topsom and by Charton. Initial- and final-state energies are analysed in terms of familiar substituent effects, such as field, delocalization and polarizability. The results show that the data correlate equally well with both sets of parameters and that there are many common features between the two methods. Both agree that resonance delocalization contributes significantly to the initial state, but has virtually no effect on the final state. In connection with this investigation we have also correlated the parameters for 31 substituents that are parameterized in the two approaches. The results of this more general study indicate some real differences between these and suggest that neither of the parameterizations incorporates all the electronic effects.

INTRODUCTION

We have recently investigated experimentally and theoretically core ionization energies for sulphur in a series of 2-substituted thiophenes.[1] The substituents



comprise CH_3, OCH_3, I, Br, Cl, CHO, CN and NO_2, and possess a wide range of electron-donating and electron-attracting properties. The results show that the variation in substituent effect is determined predominantly by the initial-state charge distribution and that the final-state charge rearrangement is very little influenced by the nature of the substituent. Furthermore, we have shown that the conclusions are not limited to the sulphur atom, but are equally well applicable to the ring carbons.

Since core ionization involves the addition of a positive charge by removal of an electron, there is a close connection between core ionization and electrophilic addition, such as protonation.[2,3] Both processes are governed by the same factors: the initial-state charge distribution and the final-state charge rearrangement, or relaxation.[4–7] The obtained result for the thiophenes therefore challenges traditional views, since resonance stabilization of the transition state (the final state of the charge addition) for electrophilic addition reactions is considered to be crucial to the understanding of both reactivity and orientation effects.[8,9]

The conclusions just mentioned are supported by correlations of core-electron energies with electronic substituent parameters using a triparametric relationship developed by Taft and Topsom.[10] However, Charton has suggested an alternative relationship which is claimed to be applicable to the entire range of electronic effects.[11] In addition Charton provides parameters for Br and I substituents, which are lacking in Taft and Tompsom's contribution. It is of interest, therefore, to present an analysis of core-electron energies in substituted thiophenes based on the two different approaches.

In general correlations between core-electron energies and electronic substituent parameters can provide useful information on initial- and final-state effects in terms of familiar substituent effects. It is, however, possible that different parameter sets are able to corre-

* Author for correspondence.

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Table 3. Results of correlations for 2-substituted thiophenes using Charton's equation:[a]

$$Q_X = L\sigma_{l,X} + D\sigma_{d,X} + E\sigma_{e,X} + h$$

Q_X	L	D	E	h	r[b]	s[c]
ΔI	1·09 ± 0·09	0·79 ± 0·08	1·1 ± 0·6	−0·02	0·992	0·06
ΔV	1·30 ± 0·09	0·64 ± 0·09	0·2 ± 0·6	0·01	0·992	0·06
ΔR	0·20 ± 0·15	−0·15 ± 0·15	−0·8 ± 1·0	0·03	0·59	0·10
ΔK	−0·7 ± 0·4	−1·1 ± 0·4	−2·5 ± 2·5	0·09	0·87	0·25
ΔI[d]	1·14 ± 0·06	0·74 ± 0·06	1·2 ± 0·4	−0·01	0·998	0·04
ΔV[d]	1·27 ± 0·06	0·68 ± 0·06	0·3 ± 0·4	0·01	0·998	0·04
ΔR[d]	0·13 ± 0·05	−0·06 ± 0·05	−1·0 ± 0·3	0·02	0·92	0·03
ΔK[d]	−0·87 ± 0·13	−0·88 ± 0·13	−3·0 ± 0·9	0·05	0·98	0·08

[a] The experimental data have been corrected for the CHO close contact (see text).
[b] Correlation coefficient.
[c] Standard error of regression.
[d] Omitting Br and I.

In our case Q_X can represent either ΔI, ΔK, ΔV or ΔR, σ_l is the localized (field and/or inductive) effect parameter and σ_d is the delocalized (resonance) parameter. These are similar but not identical to Taft and Topsom's σ_F and σ_R parameters. σ_d reflects the ability of the substituent to delocalize charge in the absence of any electronic demand from the active site; σ_e reflects the ability of the substituent to change the degree of localization of charge in response to electronic demand from the active site. The parameters $\sigma_{l,X}$, $\sigma_{d,X}$ and $\sigma_{e,X}$ for the thiophene substituents are reproduced in the last columns of Table 1. In equation (6) we have used E instead of R to denote the coefficient for electronic demand effect to avoid confusion with our choice of R for the relaxation energy.

The results according to Charton's approach are shown in Table 3. For both sets of data corrections have been made for the CHO interaction. It is seen from the first four rows of Table 3 that the correlation coefficients are not satisfactory for the full data set. However, when Br and I substituents are omitted, we see from the last four rows of Table 3 that the results are comparable in quality with those obtained from the Taft and Topsom approach. Since the correlations are particularly bad for ΔR and ΔK when Br and I are included, we conclude that the parameters do not adequately describe the high polarizability of these substituents.

The results show that there are many common features between the two different methods. In particular, we note that (1) both field (L) and delocalization (D) contribute to the initial-state potential, (2) the field and delocalization effects are very similar for ΔI and ΔV and (3) delocalization (resonance) contributes little to the relaxation. All of these results are in accord with what we have seen with the Taft/Topsom parameters.

The difference between ΔI and ΔV is mainly found in the electronic demand effect (E). This is the main contributor to ΔK and almost the sole contributor to ΔR. The relaxation energy arises from three sources: shrinkage of the valence orbitals, flow of electrons from nearby atoms to the core-ionized atom, and polarization of the surrounding atoms.[18] The electronic demand effect is related closely to the second and third of these. We see from the correlation between ΔR and σ_e that the ease of electron flow in response to demand plays a major role in determining relative relaxation energies. The negative sign of E implies an increase in relaxation energy due to this effect since all σ_e parameters considered here are negative. It is interesting to note that the ratios $E(\Delta I)/E(\Delta R)$ and $E(\Delta K)/E(\Delta R)$ are approximately -1 and $+3$ in accord with the coefficients of the ΔR terms in equations (1) and (2), respectively.

It is a striking conclusion from both of these analyses that resonance does not play a more pronounced part in the final-state relaxation process. This result challenges the traditional view since resonance stabilization of the final state has been considered to be an important contribution to chemical properties such as equilibria, reaction energies, and reaction rates. For example, the current theory of orientation in electrophilic aromatic substitution assumes that the positive Wheland intermediate[8] (the final state), and hence the transition state, is stabilized by resonance.[8,9] Our results, on the other hand, show the greater importance of the initial-state charge distribution in determining both reactivity and orientation effects of the substituents. This charge distribution affects the potential seen by the electrophile, and it is the differences in this potential that make the transition-state energies different. A more thorough discussion of the difference between our view and the traditional view is presented in Ref. 1.

COMPARISON OF THE TWO SETS OF ELECTRICAL SUBSTITUENT PARAMETERS

The results of the correlation analyses show that both parameterizations correlate well with the experimental

data. This success of both methods can result either from the small size of the data set, which does not put stringent demands on this approach, or because both parameterizations adequately describe all substituent effects. If the latter is true, then there should be a linear transformation that converts the Taft/Topsom parameters to the Charton parameters, and vice versa. To investigate this possibility we have correlated the parameters for 31 substituents that are parameterized in both approaches.[10,11] The results for the Taft/Topsom parameters as a function of Charton's parameters are:

$$\sigma_F = 0{\cdot}96\sigma_I + 0{\cdot}11\sigma_d + 0{\cdot}01\sigma_e + 0{\cdot}02 \qquad r = 0{\cdot}96$$
$$\sigma_R = 0{\cdot}13\sigma_I + 0{\cdot}70\sigma_d + 0{\cdot}73\sigma_e + 0{\cdot}02 \qquad r = 0{\cdot}96$$
$$\sigma_\alpha = 0{\cdot}17\sigma_I - 0{\cdot}46\sigma_d + 1{\cdot}46\sigma_e - 0{\cdot}46 \qquad r = 0{\cdot}58$$

For Charton's parameters as a function of these of Taft and Topsom we have:

$$\sigma_I = 0{\cdot}94\sigma_F - 0{\cdot}04\sigma_R + 0{\cdot}07\sigma_\alpha + 0{\cdot}05 \qquad r = 0{\cdot}96$$
$$\sigma_d = -0{\cdot}04\sigma_F + 1{\cdot}13\sigma_R + 0{\cdot}06\sigma_\alpha - 0{\cdot}07 \qquad r = 0{\cdot}94$$
$$\sigma_e = -0{\cdot}04\sigma_F + 0{\cdot}18\sigma_R + 0{\cdot}12\sigma_\alpha + 0{\cdot}02 \qquad r = 0{\cdot}66$$

The analysis shows that σ_F and σ_I are, as expected, closely related to each other, but not to any of the other parameters. σ_R is related primarily to the delocalization parameters σ_d. (Although the coefficients of σ_d and σ_e are comparable in the σ_R relationship, the numerical values of σ_e are much smaller than those of σ_d. Hence the primary dependence of σ_R is on σ_d). The parameter σ_d, which describes delocalization in the absence of electronic demand, correlates only with σ_R; this result is also to be expected since this delocalization is largely a resonance effect. There is, however, poor correlation ($r = 0{\cdot}58$) between the Taft/Topsom parameter for polarizability, σ_α, and the Charton parameters, suggesting that polarizability is not well described by Charton's method. This result is consistent with our observation that the Charton parameters do not account for the high polarizability of Br and I. This is not surprising since Charton's equation (equation 6) is not intended to account for polarizability.[21] In fact, Charton prefers to treat polarizability separately. Likewise, the Charton parameter, σ_e, which describes the response to electronic demand, does not correlate well with the Taft/Topsom parameters ($r = 0{\cdot}66$). It appears therefore that these two prameterizations describe different electronic effects and that a full parameterization should include both polarizability and response to electronic demand.

CONCLUSIONS

Experimental values of ΔI, ΔV, ΔR and ΔK have been correlated with electronic substituent parameters using trivariate regression analyses as developed by Taft and Topsom and by Charton. The results from both methods show that resonance delocalization involving the substituents contributes significantly to the initial-state charge distribution. However, there is virtually no influence from resonance delocalization on the final-state charge rearrangement. This result challenges the traditional view since resonance stabilization of the final state has been considered to be an important contribution to chemical properties such as equilibria, reaction energies and reaction rates.

The poor correlations for the relaxation energy and Auger kinetic energy obtained with the Charton parameters when the bromo and iodo compounds are included, indicate that this parameterization does not adequately describe the polarizability of these substituents.

Correlations of the Taft/Topsom parameters and the Charton parameters with each other show that these two parameterizations are closely related for field and resonance effects. However, they do not correlate well for effects that describe the ability of a molecule to rearrange its charge in response to electronic demand.

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REFERENCES

1. L. J. Sæthre and T. D. Thomas, *J. Org. Chem.* **56**, 3935 (1991).
2. (a) A. J. Ashe, III, M. K. Bahl, K. D. Bomben, W.-T. Chan, J. K. Gimzewski, P. G. Sitton and T. D. Thomas, *J. Am. Chem. Soc.* **101**, 1764 (1979); (b) D. W. Davis and J. W. Rabalais, *J. Am. Chem. Soc.* **96**, 5305 (1974); (c) R. L. Martin and D. A. Shirley, *J. Am. Chem. Soc.* **96**, 5299 (1974).
3. (a) R. S. Brown and A. Tse, *J. Am. Chem. Soc.* **102**, 5222 (1980); (b) R. G. Cavell and D. A. Allison, *J. Am. Chem. Soc.* **99**, 4203 (1977); (c) F. M. Benoit and A. G. Harrison, *J. Am. Chem. Soc.* **99**, 3980 (1977); (d) B. E. Mills, R. L. Martin and D. A. Shirley, *J. Am. Chem. Soc.* **98**, 2380 (1976); (e) T. X. Carroll, S. R. Smith and T. D. Thomas, *J. Am. Chem. Soc.* **97**, 659 (1975).
4. (a) L. J. Sæthre, M. R. F. Siggel and T. D. Thomas, *J. Electron Spectrosc. Relat. Phenom.* **49**, 119 (1989); (b) M. R. F. Siggel, G. S. Nolan, L. J. Sæthre, T. D. Thomas and L. Ungier, *J. Phys. Chem.* **91**, 3969 (1987); (c) G. S. Nolan, L. J. Sæthre, M. R. Siggel, T. D. Thomas and L. Ungier, *J. Am. Chem. Soc.* **107**, 6463 (1985); (d) L. J. Sæthre, T. D. Thomas and O. Gropen, *J. Am. Chem. Soc.* **107**, 2581 (1985); (e) E. J. Aitken, M. K. Bahl, K. D. Bomben, J. K. Gimzewski, G. S. Nolan and T. D. Thomas, *J. Am. Chem. Soc.* **102**, 4873 (1980).
5. (a) M. R. Siggel and T. D. Thomas, *J. Am. Chem. Soc.* **108**, 4360 (1986); (b) S. R. Smith and T. D. Thomas, *J. Am. Chem. Soc.* **100**, 5459 (1978); (c) D. W. Davis and D. A. Shirley, *J. Am. Chem. SOc.* **98**, 7898 (1976).

6. (a) M. R. F. Siggel, A. Streitwieser, Jr. and T. D. Thomas, *J. Am. Chem. Soc.* **110**, 8022 (1988); (b) T. D. Thomas, M. R. F. Siggel and A. Streitwieser, Jr. *J. Mol. Struct. (THEOCHEM)* **165**, 309 (1988); (c) T. D. Thomas, *Inorg. Chem.* **27**, 1695 (1988); (d) T. D. Thomas, T. X. Carroll and M. R. F. Siggel, *J. Org. Chem.* **53**, 1812 (1988).
7. (a) C. X. Yan and R. G. Cavell, *J. Electron Spectrosc. Relat. Phenom.* **42**, 49 (1987); (b) R. G. Cavell and R. N. S. Sodhi, *J. Electron Spectrosc. Relat. Phenom.* **41**, 25 (1986); (c) R. N. S. Sodhi and R. G. Cavell, *J. Electron Spectrosc. Relat. Phenom.* **41**, 1 (1986); (d) R. N. S. Sodhi and R. G. Cavell, *J. Electron Spectrosc. Relat. Phenom.* **32**, 283 (1983).
8. R. A. Y. Jones, *Physical and Mechanistic Organic Chemistry*, 2nd ed., pp. 215–219. Cambridge University Press, Cambridge (1984).
9. (a) R. T. Morrison and R. N. Boyd, *Organic Chemistry*, 5th ed., pp. 513–526. Allyn and Bacon, Boston (1987); (b) A. Streitwieser, Jr. and C. H. Heathcock, *Introduction to Organic Chemistry*, pp. 873–879. Macmillan, New York (1976).
10. R. W. Taft and R. D. Topsom, *Prog. Phys. Org. Chem.* **16**, 1 (1987).
11. M. Charton, *Prog. Phys. Org. Chem.* **16**, 287 (1987).
12. (a) O. Exner, in *Advances in Linear Free Energy Relationships*, edited by N. B. Chapman and J. Shorter, pp. 1–69. Plenum Press, New York (1978); (b) C. D. Johnson, *The Hammett Equation*, Cambridge University Press, Cambridge (1973); (c) H. H. Jaffe, *Chem. Rev.* **53**, 191 (1953).
13. K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Heden, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne and Y. Baer, *ESCA Applied to Free Molecules*, pp. 104–109. North-Holland Publishing Co., Amsterdam (1969).
14. R. S. Brown and A. Tse, *Can. J. Chem.* **58**, 694 (1980).
15. (a) B. J. Lindberg, S. Svensson, P.-Å. Malmquist, E. Basilier, U. Gelius and K. Siegbahn, *Chem. Phys. Lett.* **40**, 175 (1976); (b) B. J. Lindberg, S. Svensson, P.-Å. Malmquist, E. Basilier, U. Gelius and K. Siegbahn, Uppsala University, Institute of Physics, UUIP-910 (1975).
16. B. J. Lindberg, K. Helenelund, S. Hedman, L. Asplund, U. Gelius, A.-B. Hörnfeldt and S. Gronowitz, Uppsala University, Institute of Physics, UUIP-1153 (1986).
17. (a) C. D. Wagner, *J. Electron Spectrosc. Relat. Phenom.* **47**, 283 (1988); (b) H. Siegbahn and O. Goscinski, *Phys. Scr.* **13**, 225 (1976); (c) C. D. Wagner, *Faraday Discuss. Chem. Soc.* **60**, 291 (1975); (d) D. A. Shirley, *Phys. Rev.(A)* **7**, 1520 (1973).
18. T. D. Thomas, *J. Electron Spectrosc. Relat. Phenom.* **20**, 117 (1980).
19. (a) J. Shorter, *Correlation Analysis of Organic Chemistry*, Research Studies Press, Chichester (1982); (b) J. Shorter, in *Correlation Analysis in Chemistry*, edited by N. B. Chapman and J. Shorter. Plenum Press. New York (1978); (c) C. G. Swain and E. C. Lupton, Jr., *J. Am. Chem. Soc.* **90**, 4328 (1968).
20. (a) G. O. Braaten, K. Kveseth, C. T. Nielsen and K. Hagen, *J. Mol. Struct.* **145**, 45 (1986); (b) J. Fernández Bertran, E. Ortiz and L. Ballester, *J. Mol. Struct.* **17**, 161 (1973).
21. (a) M. Charton, *J. Polymer Sci.(A)* **26**, 1265 (1988); (b) M. Charton and B. I. Charton, *Bull. Soc. Chim. Fr.* 199 (1988); (c) M. Charton and H. Ziffer, *J. Org. Chem.* **52**, 2400 (1987); (d) T. K. Kwei, E. M. Pearce, J. R. Pennacchia and M. Charton, *Macromolecules* **20**, 1174 (1987).