Tetrahedron Letters,Vol.30,No.13,pp 1699-1702,1989 0040-4039/89 $3.00 + .00
Printed in Great Britain Pergamon Press plc

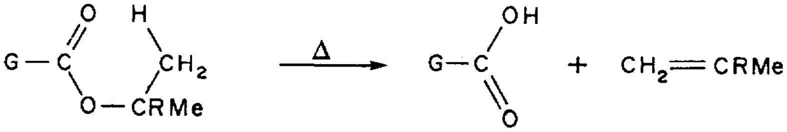
GAS-PHASE REPLACEMENT σ^0 SUBSTITUENT CONSTANTS OF HETEROARYL GROUPS[1]

Nouria A. Al-Awadi*, Rasha F. Al-Bashir, Osman M. E. ElDusouqui*

Department of Chemistry, University of Kuwait
P.O. Box 5969 Safat, 13060 Safat, Kuwait

ABSTRACT: Hammett replacement σ^0 substituent constants of pyridyl, thienyl, and furyl groups are reported for the first time from gas-phase eliminations of their *t*-butyl and isopropyl heteroarylcarboxylate esters.

Exner has recently provided a critical compilation of Hammett substituent constants and suggested that gas-phase data are of particular importance but scarce.[2] Such data would be notably free of solvent effects, protonation phenomena, and hydrogen-bonding. Replacement σ^0 constants of heteroaryl groups are so far available only from solution chemistry.[2-6] The present work therefore seems to present the first attempt at providing gas-phase data on the σ^0 parameter. The work also seems to suggest that *bona fide* heteroaryl σ^0 constants are likely to be those based on reaction (rho) constants of substituted ethanoic acids or ethanoate esters rather than their carboxylate counterparts, and that gas-phase elimination ρ parameters of the ethanoate and the carboxylate frames are interconvertible.

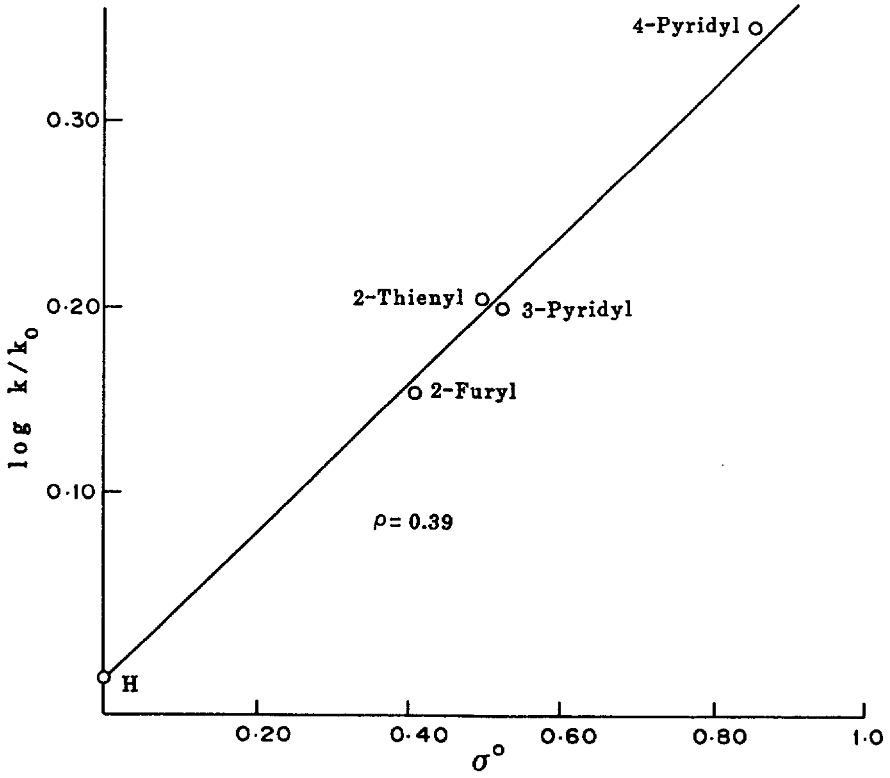


Scheme: G = phenyl, pyridyl, thienyl, or furyl group
R = H or Me substituent

Rates of the gas-phase thermal eliminations (Scheme) of six isopropyl and six *t*-butyl heteroarylcarboxylate esters together with their two reference alkyl benzoates were measured using the flow system described elsewhere.[1] From these data, replacement σ^0 substituent constants were calculated using the reaction (ρ) constants obtained from the gas-phase eliminations of the alkyl benzoate and phenylethanoate esters.

The Hammett plot (Figure) of log k/k_0 of the rates of gas-phase pyrolysis of *t*-butyl benzoate and of *t*-butyl 3- and 4-pyridyl-, 2-thienyl-, and

2-furylcarboxylates (this study) against literature[3,4] σ^0 values of these heteroaryl groups (ionization constants of substituted phenylethanoic acids and hydrolysis of substituted carboxylate esters) gave a reaction parameter $\rho = 0.39$ at 600 K. This value is the same as that obtained by Amin and Taylor[7] for the gas-phase pyrolysis of t-butyl phenylethanoate esters ($\rho = 0.39$ at 600 K). Amin and Taylor have also shown that the rho value ($\rho = 0.58$ at 600 K) of the t-butyl benzoate ester system[7] could be converted to that of the phenylethanoate system[8] using a factor (1.45) which they were able to correlate with data on benzoic and phenylethanoic acids. Structurally, the carboxylate and ethanoate systems are also interrelated: the insertion of a CH_2 unit between the (hetero)aryl moiety and the carboxylate function leads to the ethanoate frame. When factorization was extended to the analogous isopropyl ester system[7] the reaction parameter ($\rho = 0.335$ at 600 K) of isopropyl benzoate[9] was reduced to $\rho = 0.23$. It is of interest to note that the ethanoate system is expected to provide σ^0 values less susceptible to resonance interactions compared with the carboxylate frame.



In the present work two sets of gas-phase replacement σ^0 values are presented (Table) for the six heteroaryl groups under study. One set is based on the reaction constants of the isopropyl and *t*-butyl benzoate esters: $\rho = 0.335$ for the former, and 0.58 for the latter. The second set is based on the reaction constants obtained for isopropyl and *t*-butyl phenylethanoate esters: $\rho = 0.23$ and $\rho = 0.39$, respectively. For comparison purposes, the Table also contains literature σ^0 values for the same heteroaryl substituents from solution reactions. The spread between average and upper and lower limits of gas-phase σ^0 values of each individual heteroaryl group in any one of the two data sets is in the range of ± 0.02 σ^0 units. Literature σ^0 values from solution chemistry are at variance with the gas-phase data based on the ρ values of the heteroarylcarboxylate esters, but agree very well with those based on ρ constants obtained for the ethanoate esters.

Values of σ^0 from gas-phase eliminations at 600 K

Group	Alkyl Benzoates isopropyl ($\rho = 0.335$)	 *t*-butyl ($\rho = 0.58$)	Alkyl Phenylethanoates isopropyl ($\rho = 0.23$)	 *t*-butyl ($\rho = 0.39$)	Solution σ^0 constants (ref. 2-6)
3-Pyridyl	0.38	0.34	0.55	0.51	0.53;0.72
4-Pyridyl	0.61	0.60	0.88	0.89	0.85;0.94
2-Thienyl	0.37	0.35	0.53	0.52	0.50
2-Furyl	0.29	0.26	0.42	0.39	0.41
3-Thienyl	-0.089	-0.12	-0.13	-0.18	0.04
3-Furyl	-0.18	-0.17	-0.26	-0.25	0.04

We do not have as yet a rationale for the notable divergence in the σ^0 values of the 3-furyl and 3-thienyl groups except to invoke the structural framework (Scheme) through which the heteroatoms (O,S) exert their electronic effects, and to note that these centres are mesomerically electron-donating, though inductively they are electron-withdrawing. The 3-pyridyl and 4-pyridyl groups, on the other hand, are electron-withdrawing (-I; -M effects). In the case of the 2-furyl and 2-thienyl moieties, the -I effects of the O and S (most likely for proximity reasons) seem to outweigh the +M effects of these atoms. Further, the S atom has an empty d-orbital which would tend to make the thienyl groups more electron-accommodating than their furyl counterparts, a fact borne out by the comparative values of σ^0 obtained in the case of both the 2-furyl/2-thienyl and the 3-furyl/3-thienyl substituent pairs.

Acknowledgements: The authors gratefully acknowledge the support received from Kuwait University through research grant # SC032.

REFERENCES

1. Gas-phase Pyrolytic Reactions Series. For part 1, see N. A. Al-Awadi, R. F. Al-Bashir, and O. M. E. ElDusouqui, J. Chem. Soc., Perkin Trans. 2, accepted for publication: paper 8/02118J.
2. O. Exner, in "Correlation Analysis in Chemistry: Recent Advances," ed. N. B. Chapman and J. Shorter, Plenum Press, New York, 1978, Chapter 10, pp. 439 - 540.
3. Y. Otsuji, Y. Koda, M. Kubo, M. Furukawa, and E. Imoto, Nippon Kagaku Zasshi, 1959, 80, 1300.
4. J. H. Blanch, J. Chem. Soc.(B), 1966, 937.
5. G. T. Bruce, A. R. Cooksey, K. J. Morgan, J. Chem. Soc., Perkin Trans. 2, 1975, 551.
6. M. Sawada, M. Ichihara, T. Ando, and Y. Yukawa, Tetrahedron Lett., 1980, 21, 4917.
7. H. B. Amin and R. Taylor, J. Chem. Soc., Perkin Trans. 2, 1978, 1095.
8. H. B. Amin and R. Taylor, J. Chem. Soc., Perkin Trans. 2, 1975, 1802.
9. G. G. Smith, D. A. K. Jones, and D. F. Brown, J. Org. Chem., 1963, 28, 403; G. G. Smith and D. A. K. Jones, ibid, p. 3896.

(Received in UK 30 January 1989)