Tetrahedron Letters No. 3, pp 267 - 270, 1978. Pergamon Press. Printed in Great Britain.

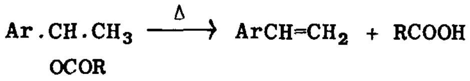
A REDEFINED σ^+-VALUE FOR THE *META*-NITRO SUBSTITUENT

By H.B. Amin and R. Taylor*

School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ, Sussex, England.

(Received in UK 21 November 1977; accepted for publication 24 November 1977)

From kinetic studies of gas-phase pyrolysis of 1-arylethyl acetates (I,R = Me) we have found[1] that in general there is an excellent correlation of



$$\underset{OCOR}{Ar.CH.CH_3} \xrightarrow{\Delta} ArCH{=}CH_2 + RCOOH$$

(I)

log $k_{rel.}$ for the elimination *vs*. σ^+-constants defined from the solvolysis of 2-aryl-2-chloropropanes[2]; ρ is -0.66 at 600K. Exceptions have been the data for the *m*-Ph[1], *m*-CF_3[3], *m*-Me[4], *m*- and *p*-$SiMe_3$[5] substituents for which σ^+-constants of 0, 0.565, -0.098, -0.165 and -0.09, respectively, are required. It is noteworthy that these values give a better correlation of *all* electrophilic substitution and related data than do the original values defined from the solvolysis.

In the above work, kinetic studies of the rate of elimination of the *m*-NO_2 ester were complicated by secondary decomposition which occurs at the temperature of the elimination. However, this is not the case for pyrolysis of the more reactive 1-arylethyl phenyl carbonates (I,R = OPh) which gives, with the exception of the *m*-nitro ester, an excellent correlation of log $k_{rel.}$ with σ^+- values with ρ = -0.84 at 600K. Correlation of the *m*-NO_2 data requires a

σ^+-value of 0.73 (cf. the literature value of 0.674[2]). A similar deviation of the log $\underline{k}_{rel.}$ value for the $\underline{m}$-NO_2 substituent is apparent from the data of Smith et al.[6] for pyrolysis of 1-arylethyl methyl carbonates. Their data require a log $f_{\underline{m}}^{NO_2}$/log $f_{\underline{p}}^{NO_2}$ value of 0.92 (cf. 0.94 from our results) whereas the existing σ^+-values predict a ratio of 0.85; data for pyrolysis of 1-arylethyl benzoates[7] also predict a high ratio. Since the pyrolysis of esters does not involve extrapolations, assumptions, corrections, the use of overlap techniques, or interference from steric hindrance to solvation[8] (all of which are involved in obtaining the literature value) we believe the latter to be in error. This view is reinforced by the following observations:

(i) Since the $\underline{m}$-NO_2 substituent cannot supply electrons conjugatively, its σ^+-value (0.674) should not be less positive than its σ-value (0.71). For the para substituent the corresponding values are 0.79 and 0.778, these differences merely reflecting small errors in establishing the ρ-factor for solvolysis of 2-aryl-2-chloropropanes on a scale relative to that for ionisation of benzoic acids. This discrepancy only should be manifest in the meta value i.e. $\sigma^+_{\underline{m}\text{-}NO_2}$ should be slightly more positive than 0.71, as is the case for the value defined by the pyrolysis.

(ii) Of the meta substituents which have a dipolar double bond and for which σ- and σ^+-values are available viz. COOEt[2], CN[2], $COCH_3$[9], and NO_2[2], only the latter substituent shows a significant difference between the meta values.

(iii) A recent statistical analysis of the Hammett equation also shows that the $\sigma^+_{\underline{m}\text{-}NO_2}$ value is anomalous.[10]

(iv) The literature value of 0.674 does not satisfactorily correlate any solution data! In protiode-silylation and -degermylation the values of log $f_{\underline{m}}^{NO_2}$/log $f_{\underline{p}}^{NO_2}$ are 0.89 and 0.91, respectively,[11] so that relative to the $\sigma^+_{\underline{p}\text{-}NO_2}$ value of 0.79, the $\sigma_{\underline{m}\text{-}NO_2}$ values required to correlate the data are 0.705 and 0.715, respectively. With the literature σ^+-value, the $\underline{m}$-NO_2 substituent deviated from the linear free energy correlation of the other data,[11] but this deviation was apparently removed by use of the Yukawa-Tsuno equation.[12] This improvement in correlation is however fortuitous, for if the difference in the σ- and σ^+-values is an experimental error rather than real, then use of this equation automatically diminishes the error. With our new value the correlation of the demetallation data for the m-NO_2 substituent is improved regardless of whether one uses the Hammett-Brown or Yukawa-Tsuno equations. In positive bromination (by HOBr)[13] for which $\rho = -6.2$, $f_{\underline{m}}^{NO_2} = 4.8 \times 10^{-5}$ so the σ^+-value required here is 0.70.

The only other reaction of this type in which the effect of the m-NO_2 substituent has been reliably measured is the decomposition of ω-diazoacetophenones.[14] Here the ratio of log $f_{\underline{m}}^{NO_2}$/log $f_{\underline{p}}^{NO_2}$ is 0.89 so the σ^+-value needed for m-NO_2 is 0.70. (On the paper describing this work the correlation with the existing σ^+-value for m-NO_2 appears to be excellent, but this is because the point is mis-plotted).

The present data provide further evidence that the pyrolysis of 1-arylethyl esters is a better model for determination of electrophilic substituent constants than is the solvolysis of 2-aryl-2-chloropropanes. In addition to the inadequacies of the latter noted above, kinetic studies usually cannot be carried out on the pure isolated compounds because of the ease with which they eliminate HCl; thus no physical characteristics were reported for either the meta- or para- nitro compounds in ref.15.

References

1. R. Taylor and G.G. Smith, *Tetrahedron*, 1963, **19**, 937.
2. L.M. Stock and H.C. Brown, *Advances in Physical Organic Chemistry*, 1963, **1**, 35.
3. R. Taylor, *J. Chem. Soc. (B)*, 1971, 622.
4. E. Glyde and R. Taylor, *J.C.S. Perkin II*, 1975, 1463.
5. E. Glyde and R. Taylor, *J.C.S. Perkin II*, 1973, 1632.
6. G.G. Smith, K.K. Lum, J.A. Kirby, and J. Posposil, *J. Org. Chem.*, 1969, **34**, 2081.
7. H.B. Amin and R. Taylor, unpublished work.
8. See E. Glyde and R. Taylor, *J.C.S. Perkin II*, 1977, 678 for discussion of the importance of this latter point.
9. R.L. Dannley and R.V. Hoffman, *J. Org. Chem.*, 1975, **40**, 2426.
10. M. Sjöström and S. Wold, *Chem. Scripta*, 1974, **6**, 115.
11. C. Eaborn and K.C. Pande, *J. Chem. Soc.*, 1961, 5082; C. Eaborn and P.M. Jackson, *J. Chem. Soc. (B)*, 1969, 21.
12. Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Japan*, 1959, **32**, 971.
13. P.B.D. de la Mare and I.C. Hilton, *J. Chem. Soc.*, 1962, 997.
14. Y. Ysuno, T. Ibata and Y. Yukawa, *Bull. Chem. Soc. Japan*, 1959, **32**, 960.
15. Y. Okamoto and H.C. Brown, *J. Am. Chem. Soc.*, 1957, **79**, 1909.