Electrophilic Aromatic Reactivities *via* Pyrolysis of 1-Arylethyl Acetates. Part XI.[1] The σ^+ Value for the *m*-Methyl Substituent

By **Ernest Glyde** and **Roger Taylor,*** School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ, Sussex

The rates of gas-phase elimination of acetic acid from 1-(*m*-methylphenyl)ethyl acetate together with that of 1-phenylethyl acetate between 613.8 and 666.1 K have been determined. From these data a new value of $\sigma^+_{m\text{-Me}}$ of −0.098 is obtained. This gives a much better correlation of the effect of the *m*-methyl substituent in electrophilic substitutions in solution than does the existing value of −0.066 which is considerably in error. The new value shows that there is a significant relay of polarisability effects to the *meta*-position in toluene and derivatives.

THE *m*-methyl substituent, because of the accessibility of toluene and its derivatives, is one of the groups most commonly used in evaluating electrophilic aromatic substitutions and related reactions in terms of Hammett correlations; accurate knowledge of its σ^+ value is therefore desirable. The value determined from solvolysis of 2-aryl-2-chloropropanes [2] (−0.066) has hitherto been regarded as satisfactory because of its similarity to the $\sigma_{m\text{-Me}}$ value (−0.069).[2] However, the difference between σ^+ and σ for the *p*-methyl substituent is quite large (0.14) and it is unreasonable to assume that none of this conjugative electron release is relayed to the *meta*-position.

The pyrolysis of 1-arylethyl acetates gives (with the exception of three substituents) an excellent correlation with σ^+ values.[3,4] The *m*-Ph value of 0.109 (ref. 2) was indicated by this reaction to be much too high [5] and a new value of +0.05 ± 0.01 was subsequently determined.[6] The gas-phase value of 0.565 for *m*-CF_3 gave a better correlation of all electrophilic substitutions and related reactions [7] than did the standard value [2] of 0.52. The gas-phase values for the *meta*- and *para*-$SiMe_3$ substituents (−0.16 and −0.09) correctly predicted the reactivity patterns in electrophilic substitution whereas the standard values [2] (+0.01 and +0.02) did not.

While investigating the additivity of methyl substituent effects in pyrolysis of 1-arylethyl acetates we observed that the effects of *m*-methyl groups seemed to be significantly larger than predicted by the σ^+ value. Our analysis of earlier work [8] on the reactivity of the 3,5-dimethyl ester indicated that a value for $\sigma^+_{m\text{-Me}}$ of *ca.* −0.1 would be needed. We therefore prepared 1-(*m*-methylphenyl)ethyl acetate and measured its rate of elimination together with that of 1-phenylethyl acetate at a number of temperatures over a 50 K range.

RESULTS AND DISCUSSION

The kinetic data are given in the Table; these gave excellent Arrhenius plots as indicated by the correlation coefficients, and the data for the unsubstituted compound agreed within experimental error with results previously obtained in this work.[3] The log $k_{\text{rel.}}$ value at 600 K (at which temperature ρ is −0.66) leads to a σ^+ value of −0.098 ± 0.006 (error calculated for ±1% error in the derived relative rate).

Pyrolysis of compounds $RC_6H_4{\cdot}CH(OAc){\cdot}CH_3$

	$10^3k/s^{-1}$	
T/K	R = H	*m*-Me
666.1	28.8	
665.9		33.2
642.4	8.34	
642.0		9.76
627.7	3.67	4.36
613.8	1.735	1.94
Correlation coeff.	0.999 86	0.999 97
log (A/s^{-1})	12.8	13.0
E/kcal mol^{-1}	44.0	44.6
S/cal mol^{-1} K^{-1}	−1.36	−0.44
log k/k_0 (at 600 K)	0	0.065

The value of $\sigma^+_{m\text{-Me}}$ which we obtain agrees well with the value indicated by the work of Smith and White [8] and our work on additivity effects as noted above. However it differs considerably from the previously accepted value so we felt it necessary to calculate the individual values for each reaction for which data are available. The average value from side-chain carbocation reactions (reactions 1, 2, 4, 9, 10, 13, 24—27, 29, and 30 in the review of Yukawa and Tsuno [9]) is −0.086. For electrophilic substitutions, *viz.* hydrogen exchange ($CF_3{\cdot}CO_2H$ and H_2SO_4), protode-silylation, -germylation, -stannylation, bromo- and mercuri-desilylation, acetylation, benzoylation, mercuriation, sulphonation, molecular bromination (aq. HOAc), molecular chlorination (HOAc), iodination ($ZnCl_2$–HOAc), positive bromination, and positive chlorination,[10] the average value is −0.085. Moreover the individual values for electrophilic substitution range from −0.071 to −0.105 and tend to increase with increasing ρ factor for the reaction, supporting our proposal that

---

[1] Part X, R. Taylor, *J.C.S. Perkin II*, 1975, 277.

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

[3] E. Glyde and R. Taylor, *J.C.S. Perkin II*, 1973, 1632, and earlier papers in this series.

[4] R. Taylor and G. G. Smith, *Tetrahedron*, 1963, **19**, 937.

[5] R. Taylor, G. G. Smith, and W. H. Wetzel, *J. Amer. Chem. Soc.*, 1963, **84**, 4817.

[6] L. M. Stock and H. C. Brown, *J. Amer. Chem. Soc.*, 1962, **84**, 1242.

[7] R. Taylor, *J. Chem. Soc.* (*B*), 1971, 622; W. D. Totherow and G. J. Gleicher, *J. Amer. Chem. Soc.*, 1969, **91**, 7150.

[8] G. G. Smith and D. V. White, *J. Org. Chem.*, 1964, **29**, 3533.

[9] Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Japan*, 1959, **32**, 971, Table 1.

[10] The relevant data may be found in R. O. C. Norman and R. Taylor, ' Electrophilic Substitution in Benzenoid Compounds,' Elsevier, Amsterdam, 1965.

the substituent is susceptible to polarisability requirements. A second point is that in hydrogen exchange (for which data are very accurately known since one does not have to rely on estimations of yields of minor components from gas chromatographic traces—see the effect of this in nitration for example [10]) the derived values are −0.093 and −0.098, in excellent agreement with our new value.

This discrepancy has not previously been noted because the closeness of the *m*-Me point to the origin in Hammett analyses means that seemingly small deviations tend to be ignored when in fact they are relatively large; the same error is inherent in verifications of the Extended Selectivity Relationship and one of us has drawn attention to this elsewhere.[11]

Since the difference between σ and σ^+ is now significant it is evident that for reactions of low demand for resonance stabilisation of transition states, the Yukawa–Tsuno analysis is best applied to the *m*-Me substituent as well. Thus for example the effective values in proto-desilylation, -degermylation, and -destannylation would be −0.087, −0.085, and −0.079, respectively.

EXPERIMENTAL

The kinetic technique has been described previously; [12] rate coefficients could be duplicated to within ±1%, and kinetic plots showed first-order linearity to beyond 95% of reaction.

1-Phenylethyl acetate was available from previous work.[1]

1-(3-*Methylphenyl*)*ethyl Acetate*.—The Grignard reagent from *m*-bromotoluene was treated with redistilled acetaldehyde to give, after normal work-up, 1-(3-methylphenyl)-ethyl alcohol (75%). G.l.c. analysis indicated this crude product to be at least 92% pure so it was acetylated directly with pyridine and acetic anhydride to give, after normal work-up and fractional distillation, 1-(3-*methylphenyl*)*ethyl acetate* (26% based on bromotoluene), b.p. 103 °C at 7.0 mmHg (Found: C, 72.6; H, 8.4. $C_{11}H_{14}O_2$ requires C, 72.4; H, 8.5%).

[5/558 *Received*, 21*st March*, 1975]

---

[11] R. Taylor, Chem. Soc. Specialist Periodical Report, 'Aromatic and Heteroaromatic Chemistry,' 1975, vol. 3, p. 220.

[12] R. Taylor, *J. Chem. Soc.* (*B*), 1968, 1397.